Acerca de este libro

Esta es una copia digital de un libro que, durante generaciones, se ha conservado en las estanterías de una biblioteca, hasta que Google ha decidido escanearlo como parte de un proyecto que pretende que sea posible descubrir en línea libros de todo el mundo.

Ha sobrevivido tantos años como para que los derechos de autor hayan expirado y el libro pase a ser de dominio público. El que un libro sea de dominio público significa que nunca ha estado protegido por derechos de autor, o bien que el período legal de estos derechos ya ha expirado. Es posible que una misma obra sea de dominio público en unos países y, sin embargo, no lo sea en otros. Los libros de dominio público son nuestras puertas hacia el pasado, suponen un patrimonio histórico, cultural y de conocimientos que, a menudo, resulta difícil de descubrir.

Todas las anotaciones, marcas y otras señales en los márgenes que estén presentes en el volumen original aparecerán también en este archivo como testimonio del largo viaje que el libro ha recorrido desde el editor hasta la biblioteca y, finalmente, hasta usted.

Normas de uso

Google se enorgullece de poder colaborar con distintas bibliotecas para digitalizar los materiales de dominio público a fin de hacerlos accesibles a todo el mundo. Los libros de dominio público son patrimonio de todos, nosotros somos sus humildes guardianes. No obstante, se trata de un trabajo caro. Por este motivo, y para poder ofrecer este recurso, hemos tomado medidas para evitar que se produzca un abuso por parte de terceros con fines comerciales, y hemos incluido restricciones técnicas sobre las solicitudes automatizadas.

Asimismo, le pedimos que:

+ *Haga un uso exclusivamente no comercial de estos archivos* Hemos diseñado la Búsqueda de libros de Google para el uso de particulares; como tal, le pedimos que utilice estos archivos con fines personales, y no comerciales.
+ *No envíe solicitudes automatizadas* Por favor, no envíe solicitudes automatizadas de ningún tipo al sistema de Google. Si está llevando a cabo una investigación sobre traducción automática, reconocimiento óptico de caracteres u otros campos para los que resulte útil disfrutar de acceso a una gran cantidad de texto, por favor, envíenos un mensaje. Fomentamos el uso de materiales de dominio público con estos propósitos y seguro que podremos ayudarle.
+ *Conserve la atribución* La filigrana de Google que verá en todos los archivos es fundamental para informar a los usuarios sobre este proyecto y ayudarles a encontrar materiales adicionales en la Búsqueda de libros de Google. Por favor, no la elimine.
+ *Manténgase siempre dentro de la legalidad* Sea cual sea el uso que haga de estos materiales, recuerde que es responsable de asegurarse de que todo lo que hace es legal. No dé por sentado que, por el hecho de que una obra se considere de dominio público para los usuarios de los Estados Unidos, lo será también para los usuarios de otros países. La legislación sobre derechos de autor varía de un país a otro, y no podemos facilitar información sobre si está permitido un uso específico de algún libro. Por favor, no suponga que la aparición de un libro en nuestro programa significa que se puede utilizar de igual manera en todo el mundo. La responsabilidad ante la infracción de los derechos de autor puede ser muy grave.

Acerca de la Búsqueda de libros de Google

El objetivo de Google consiste en organizar información procedente de todo el mundo y hacerla accesible y útil de forma universal. El programa de Búsqueda de libros de Google ayuda a los lectores a descubrir los libros de todo el mundo a la vez que ayuda a autores y editores a llegar a nuevas audiencias. Podrá realizar búsquedas en el texto completo de este libro en la web, en la página `http://books.google.com`

This is a reproduction of a library book that was digitized by Google as part of an ongoing effort to preserve the information in books and make it universally accessible.

Google™ books

https://books.google.com

B 561,525 DUPL

Google

1837
ARTES VERITAS SCIENTIA
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
TUEBOR
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

PHYSICS LIBRARY

Physics Lib.
QC
1
.P5821

PROCEEDINGS

OF THE

PHYSICAL SOCIETY OF LONDON

From December 1925 to August 1926

VOL. XXXVIII.

LONDON:
FLEETWAY PRESS LTD.,
3-9, DANE STREET, HIGH HOLBORN, W.C 1.
MDCCCCXXVI.

LONDON:
FLEETWAY PRESS LTD.,
DANE STREET, HOLBORN, W.C.1

For Physics Lab.
Gen
Lapon

CONTENTS

VOL. XXXVIII.

PAGE

Proceedings at Meetings vii

The Influence of Strain on the Thomson Effect. By HUGH E. SMITH, B.Sc. 1

On the Flashing of Certain Types of Argon-Nitrogen Discharge Tubes. By WILLIAM CLARKSON, M.Sc., A.Inst.P. 10

On the Viscosity of Ammonia Gas. By S. G. EDWARDS, A.R.C.S., B.Sc., D.I.C., and B. WORSWICK, A.R.C.S., B.Sc., D.I.C. 16

Valve Maintained Tuning Forks. By T. G. HODGKINSON, A.M.I.E. .... 24 ✓

The Times of "Sudden Commencements" (S.C.s) of Magnetic Storms: Observation and Theory. By C. CHREE, Sc.D., LL.D., F.R.S. 35

The Measurement of Temperature by Thermocouples in Unequally Heated Enclosures. By W. MANDELL, B.Sc. 47

Photo-electric Radiation Pyrometer. By Prof. F. A. LINDEMANN, F.R.S., and T. C. KEELEY 69

Measurement of Ozone in the Earth's Atmosphere. By G. M. B. DOBSON, D.Sc., and D. N. HARRISON, B.A. 74

The Absorption Coefficient for Slow Electrons in Mercury Vapour. By ROBERT B. BRODE, B.Sc., Ph.D. 77

Two New Types of High Vacuum Gauge. By E. BOLTON KING 80

An Application of Spectro-Photography to the Measurement of High Temperatures. By I. O. GRIFFITH, M.A. 85

On the Bending of Crystals. By C. H. BOSANQUET 88

Demonstration of the Kinetic Properties of a Gas Jet. By Dr. J. S. G. THOMAS ... 92

Atomic Dimensions. By R. G. LUNNON, M.A., M.Sc. 93

On Edge-Tones. By W. E. BENTON, B.Sc. 109

The Spectroscopic Detection of Minute Quantities of Mercury. By J. J. MANLEY, M.A. 127

PAGE

On the Storage of Small Quantities of Gas at Low Pressures. By J. J. MANLEY, M.A. 129

The Effect of Rolling on the Crystal Structure of Aluminium. By E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A. 132

The Spreading of One Liquid on the Surface of Another. By R. S. BURDON, B.Sc., A.Inst.P. 148

On the Advance of Perihelion of Mercury. By J. T. COMBRIDGE, M.A., M.Sc. 161

Demonstration of an Instrument for Imitating the Eastward Deviation of Bodies Falling from a Great Height. By G. R. MATHER 168

Critical Discussion of the Determinations of the Mechanical Equivalent of Heat. By Prof. T. H. LABY, M.A., Sc.D., F.Inst.P. 169

The Present Status of Theory and Experiment Relating to Specific Heats and the Chemical Constant. By F. IAN G. RAWLINS 176

On the "Hyperbola" Method for the Measurement of Surface Tensions. By A. FERGUSON, M.A., D.Sc., and I. VOGEL, B.Sc. 193

The Application of Radiography to the Study of Capillarity. By E. A. OWEN, M.A., D.Sc., and A. F. DUFTON, M.A., D.I.C. 204

The Effects of Torsion upon the Thermal and Electrical Conductivities of Aluminium, with Special Reference to Single Crystals. By J. E. CALTHROP, M.A., M.Sc. 207

Variations in the Thermionic and Photo-Electric Emission from Platinum and Tungsten. By T. H. HARRISON, B.Sc. 214

The Analogy between Ripples and Acoustical Wave Phenomena. By A. H. DAVIS, D.Sc. 234

On the Evaporative Losses of Vacuum-Jacketed Vessels of the Dewar Type. By R. M. ARCHER, A.R.C.Sc., B.Sc., M.I.E.E. 247

Demonstration of the Application of the Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material. By J. J. HARTLEY, M.Eng., M.Sc., A.M.I.C.E., and R. H. RINALDI 273

Demonstration Surface Tension Phenomena. By EDWIN EDSER 274

Demonstration of Surface Tension Phenomena. By Prof. C. R. DARLING 275

Obliquity Corrrections in Radium Estimation. By IVOR BACKHURST, M.Sc. 277

Viscosity of Water at Low Rates of Flow Determined by a Method of Thermal Convection. By ALBERT GRIFFITHS, D.Sc., and P. C. VINCENT, B.Sc. 291

PAGE

The Properties of Mutual Inductance Standards at Telephonic Frequencies. By L. Hartshorn, A.R.C.S., B.Sc., D.I.C. 302

A Note on λ 4722 of Bismuth and the Nature of "Raies Ultimes." By A. L. Narayan and K. R. Rao 321

The Distribution of Intensity in a Positive Ray Spectral Line. By M. C. Johnson, M.A., M.Sc. 324

Demonstration of Some Simple Experiments with Thermionic Valves. By E. H. Rayner, Sc.D. 335

Static and Isotropic Gravitational Fields. By G. Temple, Ph.D 337

On the Diffraction of Light by Spherical Obstacles. By Prof. C. V. Raman, F.R.S., and K. S. Krishnan 350

On the Absorption and Series Spectra of Nickel. By Prof. A. L. Narayan and K. R. Rao 354

The Influence of Electrolytes in Electro-Endosmosis. By H. C. Hepburn, B.Sc. ... 363

The Latent Heat of Fusion of Some Metals. By J. H. Awbery, B.Sc., and Ezer Griffiths, D.Sc. 378

The Piezo-Electric Quartz Resonator and its Equivalent Electric Circuit. By D. W. Dye, B.Sc. .... 399 ✓

The Characteristics of Electrostatic Machines. By F. J. Evans 459

The Refraction and Dispersion of Gaseous Carbon Disulphide. By H. Lowery, M.Sc. 470

On the Use of Invar Steel for Precision Balances. By J. J. Manley, M.A. 473

On the Scattering Power of Oxygen and Iron for X-Rays. By A. A. Claassen... 482

Index 489

PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY OF LONDON

SESSION 1925-1926.

Except where a statement to the contrary occurs, the meetings were held at the Imperial College of Science, the President being in the Chair.

October 23, 1925.

The following Papers were read :—

1. "The Influence of Strain on the Thomson Effect," by H. E. **Smith**, B.Sc.

2. "The Measurement of Temperature by Thermocouples in Unequally Heated Enclosures," by W. **Mandell**, B.Sc.

3. "On the Flashing of Certain Types of Argon-Nitrogen Discharge Tubes," by W. **Clarkson**, M.Sc.

November 13, 1925.

Dr. W. H. **Eccles** proposed and Dr. E. H. **Rayner** seconded a vote of congratulation to Mr. F. E. **Smith** on the recent presentation to him of the Hughes Medal of the Royal Society. The vote was carried by acclamation.

The following Papers were read :—

1. "On the Viscosity of Ammonia Gas," by R. G. **Edwards**, A.R.C.S., B.Sc., D.I.C., and B. **Worswick**, A.R.C.S., B.Sc., D.I.C.

2. "Valve Maintained Tuning Forks without Condensers," by T. G. **Hodgkinson**, A.M.I.E.E.

3. "The Times of Sudden Commencements of Magnetic Storms; Observation and Theory," by Dr. C. **Chree**, F.R.S.

A **Demonstration** of "The Kinetic Properties of a Gas Jet" was given by Dr. J. S. G. **Thomas**.

November 27, 1925.

The following Papers were read :—

1. "Atomic Dimensions," by R. G. LUNNON.

2. "On Edge Tones" (I), by W. E. BENTON, B.Sc.

3. "The Spectroscopic Detection of Minute Quantities of Mercury," by J. J. MANLEY, M.A.

4. "On the Storage of Small Quantities of Gas at Low Pressures," by J. J. MANLEY, M.A.

A DEMONSTRATION of "An Instrument for Imitating the Eastward Deviation of Bodies Falling from a Great Height" was given by Mr. G. R. MATHER.

December 11, 1925.

The following Papers were read :—

1. "The Effect of Rolling on the Crystal Structure of Aluminium," by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A.

2. "On the Spreading of One Liquid on the Surface of Another," by R. S. BURDON, B.Sc., A.Inst.P.

3. "On the Advance of the Perihelion of Mercury," by J. T. COMBRIDGE, M.A., M.Sc.

January 5, 6 and 7, 1926.

The Annual Exhibition of Apparatus was held by the Physical Society of London and the Optical Society from 3-6 p.m. and from 7-10 p.m. each day.

Discourses were given as follows :—

At 8 p.m., January 5, "The Search for Ultra-Microscopic Organisms," by J. E. BARNARD, F.R.S.

At 8 p.m., January 6, "The Mechanical Design of Instruments," by Prof. A. F. C. POLLARD, A.R.C.S., A.M.I.E.E.

At 8 p.m., January 7, "Electrical Listening," by Major W. S. TUCKER, D.Sc.

January 22, 1926.

The following Papers were read :—

1. "A Critical Discussion of the Determinations of the Mechanical Equivalent of Heat," by Prof. T. H. LABY, M.A., Sc.D., F.Inst.P.

2. "The Present Status of Theory and Experiment relating to Specific Heats and the Chemical Constant," by F. IAN G. RAWLINS, B.A.

After the first Paper Prof. LABY gave an account of experiments made by himself and Mr. E. D. HERCUS on a direct determination of the Mechanical Equivalent of Heat.

February 12, 1926.

Annual General Meeting.

GENERAL BUSINESS.

The Report of the Council and that of the Treasurer were presented and unanimously adopted.

REPORT OF THE COUNCIL.

During the year fourteen ordinary Science Meetings have been held at the Imperial College of Science. In addition, by kind invitation of Prof. F. A. Lindemann, about 180 Fellows of the Society and their friends visited Oxford on July 4. Prof. Lindemann entertained the visitors to lunch in Christ Church Hall and to tea in Wadham College Hall. The Clarendon Laboratory was open for inspection, and a Science Meeting was held there after tea, when several Papers were read by workers in the Laboratory.

At the Science Meetings held during the year 38 Papers were presented and 12 Demonstrations were given.

Mr. F. E. Smith gave his Presidential Address on February 13. The subject was "A System of Electrical Measurements," and the address was illustrated by experiments.

Prof. Willy Wien, of Munich, delivered on April 24 the Tenth Guthrie Lecture on "Recent Researches in Positive Rays." About 130 Fellows and visitors were present.

On May 22 Prof. L. S. Ornstein, of Utrecht, gave a lecture to the Society on "The Intensity of Spectral Lines: Measurement and Theory."

The average attendance at the meetings of the Society was 64.

The Fifteenth Annual Exhibition of Scientific Apparatus, arranged jointly by the Physical and Optical Societies, was held, through the courtesy of the Governing Body, at the Imperial College, on January 7 and 8. Exhibits were arranged by sixty firms, and the attendance was large, probably about 3,000. Discourses were given by

Mr. F. Twyman on "Some Experiments with Interferometers," and by Mr. C. F. Elwell on "Talking Motion Pictures."

Arrangements have been made for the extension of the scope of future Exhibitions by the inclusion, in addition to the ordinary trade exhibits, of new groups illustrating the results of recent physical research and improvements in laboratory practice, lecture experiments, and famous historical experiments in physics. The Exhibition will remain open for a third day, on which the general public will be admitted. These changes take effect in January, 1926.

Dr. D. Owen and Dr. J. H. Vincent have been appointed representatives of the Society on the Board of the Institute of Physics, and Mr. T. Smith and Dr. D. Owen on the Science Abstracts Committee. Mr. F. J. W. Whipple has been re-appointed as the Society's representative on the Geophysical Committee of the Royal Astronomical Society.

At the invitation of the National Institute for the Blind, the Council has nominated Dr. W. S. Tucker as a member of the Technical and Research Committee of the Institute.

Dr. C. E. Guillaume, Honorary Fellow, acted as delegate of the Society at the International Conference on the use of Esperanto, in Paris, May 14-16; and Dr. E. A. Owen was the official representative of the Society at the International Congress on Radiology in London, July 1-4.

Messages of congratulation have been sent to the Russian Academy of Science on the attainment of its bicentenary, and to Prof. H. A. Lorentz, the senior Honorary Fellow of the Society, on the occasion of his Doctorate Jubilee.

The numerous copies of the Proceedings of the Society which came into its possession through the kindness of Lady Thorpe have been presented to the Library of the University College of North Wales, Bangor. The Council also presented a bound copy of Wheatstone's Papers to the Gloucester Public Library on the occasion of the unveiling of the Wheatstone Memorial.

The Council has awarded the Third Duddell Medal to Mr. Albert Campbell. This medal will be presented at the Annual General Meeting.

Negotiations with the Institution of Electrical Engineers for a new agreement in relation to Science Abstracts have been carried on, and are nearly complete.

The Council has appointed a sub-committee to inquire into the desirability of changing the name of the Society, and now has the report of the sub-committee under consideration.

Through the courtesy of the Governing Body, it has been possible to resume the use of the original room in the Imperial College for the purposes of the business of the Society.

The Society has to record with regret the deaths of Prof. A. Liveing, Prof. Sir Edward Thorpe, Sir William Barrett, Dr. E. Hopkinson, Prof. E. H. Barton and Mr. H. St. G. Anson. Sir William Barrett was one of the few remaining Original Fellows, and took a prominent part in founding the Society. He was a Life Fellow. Prof. Liveing, Dr. Hopkinson and Sir Edward Thorpe were also Life Fellows of long standing, having been elected in 1879, 1882 and 1885 respectively. Prof. Barton was elected in 1892, and had served on the Council and as Vice-President; Mr. St. G. Anson was one of the youngest Fellows; he was elected in 1923.

The number of Honorary Fellows on the Roll on December 31, 1925, shows an increase to 11, Prof. Willy Wien having been added at the last Annual General Meeting. The number of Ordinary Fellows and Students at the same date stands at 656 (Fellows 640, Students 16). During the year 55 new Fellows were elected, 10 being transfers from Student Membership, and nine Students were admitted.

REPORT OF THE TREASURER.

The financial position of the Society may be considered as satisfactory, the Income having exceeded the Expenditure.

The Council is indebted to the Council of the Royal Society for a grant of £100 towards the cost of publications. It has also to acknowledge the generous attitude adopted by the Institution of Electrical Engineers towards the cost of the publication of "Science Abstracts" for 1924.

The Council has decided that in future the Entrance Fees received from Fellows shall not be treated as Income, but shall be invested in the same way as the Life Composition Fees. The Entrance Fees received during the past year have therefore been placed to the Accumulated Fund.

£150 Southern Railway 5 per cent. Debenture Stock was purchased, this amount approximately covering the Composition Fees of Fellows elected during 1924 and 1925.

The investments have been valued at market prices through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank. Owing to the fall in value of securities during the year, the market value of the Society's investments (including the Trust Funds) decreased during the twelve months by £195 15s. 5d.

DISCUSSION OF THE REPORTS.

The retiring **PRESIDENT**, inviting a general discussion on the reports, said that he hoped the new Council would continue to arrange visits to centres of learning other than London from time to time. The meetings held by the Society at Oxford in 1925, and Cambridge in 1924, had been most successful.

Dr. **LEWIS SIMONS** reminded the President that the latter had once put forward a proposal that the Societies concerned in Physics should combine to provide a joint home of their own. The financial difficulties would be very great, but he felt that the proposal should not be lost sight of.

Sir **RICHARD PAGET** inquired what the cost of such a scheme would be.

Dr. C. **CHREE** said that the Royal Meteorological Society had found that the cost of a suitable building in Kensington was about £6,000.

INCOME AND EXPENDITURE ACCOUNT.

From January 1st to December 31st, 1925.

1924. £ *s.* *d.*	EXPENDITURE.	£ s. d.	£ s. d.
	"Science Abstracts," 1925 (Inst. El. Eng.)	417 0 0	
281 0 0	Ditto, 1924 (balance)	96 0 0	513 0 0
	Ordinary Publications :—		
786 14 2	"Proceedings"	892 1 1	
63 11 5	"Bulletin"	70 5 0	
102 14 2	General	102 8 7	1,064 14 8
87 6 2	Postage of Publications		93 1 2
61 14 4	Reporting	62 1 1	
26 19 4	Refreshments and Expenses of Ordinary Meetings	29 6 3	
181 11 0	Expenses of Exhibition held jointly with the Optical Society	203 14 0	
28 8 10	Secretary's Expenses	17 11 4	
18 14 1	Treasurer's Expenses	10 9 6	
7 15 0	Periodicals and Library	8 5 1	
1 15 0	Insurance	1 15 0	
2 2 0	Registered Address	2 2 0	
0 10 6	Cheque Books	0 5 2	
4 12 0	Advertising.		
15 12 0	Accountancy Charges and Clerical Assistance	20 15 0	
	Sundry Expenses	2 15 9	359 0 2
10 0 0	Guthrie Lecture (Honorarium)	20 0 0	
	Donation to 1926 Optical Convention	10 10 0	
	Donation to Lorentz Memorial	5 5 0	35 15 0
20 0 0	Donation to Institute of Physics.		
25 0 0	Grant to the Widow of A. V. Parke.		
277 12 8	Excess of Income over Expenditure		90 7 1
£2,003 15 8			£2,155 18 1

1924. £ *s.* *d.*	INCOME.	£ s. d.	£ s. d.
866 5 8	Subscriptions by Fellows*	954 0 10	
9 9 0	" Voluntary†	9 9 0	
8 18 6	" by Students	8 18 6	
10 10 0	Institute of Physics.		
4 12 6	Arrears.		
36 0 0	Subscriptions for "Science Abstracts" and Advance Proofs	42 11 0	1,014 19 4
935 15 8			
639 17 7	Sale of Publications (Fleetway Press, Ltd.)		605 6 10
	Dividends :—		
43 7 4	London Midland & Scottish Railway	43 14 4	
7 0 0	Metropolitan Board of Works	7 0 0	
9 6 0	Lancaster Corporation Stock	9 9 0	
14 4 11	New South Wales Stock	10 0 2	
23 9 5	Southern Railway	23 15 1	
15 10 0	London & North Eastern Railway	15 12 6	
17 10 0	India 3½%	17 10 0	
20 3 0	4% Funding Loan	20 9 6	
35 0 0	5% War Loan	35 0 0	
1,761 3 11		182 10 7	
20 0 0	*Less :* Transferred to Duddell Memorial Trust Fund	20 0 0	
1,741 3 11			162 10 7
58 17 3	Income Tax repayable one year to December 31, 1925		40 0 0
5 5 4	Interest on Deposit Account		9 19 8
8 6 8	Optical Society for Share of Exhibition Expenses		4 5 10
138 18 6	Exhibitors' Payments on account of Exhibition Catalogues		193 2 6
	Royal Society Grant for Publications		100 0 0
	Royal Meteorological Society for Share in the cost of the Publication of the Discussion on "Ionization of the Atmosphere, etc."		25 13 4
5 0 0	Translating Dr. Jeans' Report.		
46 4 0	Entrance Fees.		
£2,003 15 8			£2,155 18 1

ROBERT S. WHIPPLE, *Honorary Treasurer.*

Audited and found correct,

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

January 27th, 1926.

---

* Fifty-seven Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total discount amounting to £23 4s. 8d.

† "Voluntary Subscriptions" are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AT DECEMBER 31ST, 1925.

LIABILITIES.

	£	s.	d.	£	s.	d.
Accumulated Fund:—						
Balance as per last account	1,880	5	4			
Entrance Fees, 1925	31	10	0			
	1,911	15	4			
Less Decreased Value of Investments	165	15	5			
	1,745	19	11			
Add Excess of Income over Expenditure, 1925	90	7	1			
				1,836	7	0
Life Compositions:—						
Balance as per last Account	2,154	0	0			
Added during year	51	10	0			
				2,205	10	0
Duddell Memorial Trust Fund as per last Account	432	12	9			
Less Decreased Value of Investments	4	0	0			
				428	12	9
W. F. Stanley Trust Fund as per last Account	449	0	0			
Less Decreased Value of Investments	26	0	0			
				423	0	0
Sundry Creditors				529	17	1
Subscriptions paid in advance				21	0	0
				£5,444	6	10

ASSETS.

	£	s.	d.	£	s.	d.
Investments at Market Value on date:—						
£399 London Midland & Scottish Railway 4 per cent. Debenture Stock	323	0	0			
£1,000 London Midland and Scottish Railway 4 per cent. Preference Stock	735	0	0			
£200 Metropolitan Board of Works 3½ per cent. Stock	188	0	0			
£400 Lancaster Corporation 3 per cent. Redeemable Stock	280	0	0			
£254 2s. 9d. New South Wales 5 per cent. 1935-55	252	0	0			
£300 Southern Railway Preferred Ordinary Stock	228	0	0			
£442 Southern Railway Deferred Ordinary Stock	195	0	0			
£150 Southern Railway 5 per cent. Debenture Stock	149	0	0			
£500 London & North Eastern Railway 4 per cent. Debenture Stock	380	0	0			
£500 India 3½ per cent. Stock	332	0	0			
£650 4% Funding Loan, 1960-90	558	0	0			
£300 5% War Loan 1929/47 inscribed, "A" Account	301	0	0			
£400 5% War Loan 1929/47 inscribed, "B" Account (Duddell Memorial Fund)	402	0	0			
				4,323	0	0
Stock of Publications (as per Treasurer's valuation)				400	0	0
Subscriptions due	29	1	9			
Due from Fleetway Press (Contra)	177	10	0			
Due from Customs and Excise for Income Tax Reclaim	32	4	2			
				238	15	11
Cash at Bankers, Deposit Account	300	0	0			
Cash at Bankers, Current Account	171	12	7			
Cash in hand of Treasurer	9	13	0			
Petty Cash in hand	1	5	4			
				482	10	11
				£5,444	6	10

ROBERT S. WHIPPLE, *Honorary Treasurer.*

Audited and found correct,

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

January 27th, 1926.

Note.—The value of the Society's library has not been brought into the Balance Sheet.

LIFE COMPOSITION FUND AT DECEMBER 31ST, 1925.

	£	s.	d.
128 Fellows paid £10	1,280	0	0
3 Fellows paid £15	45	0	0
1 Fellow paid £20	20	0	0
1 Fellow paid £20 10s.	20	10	0
13 Fellows paid £21	273	0	0
18 Fellows paid £31 10s.	567	0	0
164	£2,205	10	0

W. F. STANLEY TRUST FUND (FOR THE "BULLETIN").

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	228	0	0	Carried to Balance Sheet	423	0	0
£442 Southern Railway Deferred Ordinary Stock	195	0	0				
	£423	0	0		£423	0	0

DUDDELL MEMORIAL TRUST FUND.

CAPITAL

	£	s.	d.		£	s.	d.
£400 War Loan 5% 1929/47 inscribed Stock	402	0	0	Carried to Balance Sheet	402	0	0

REVENUE.

	£	s.	d.		£	s.	d.
Balance at 31st December, 1924	26	12	9	Honorarium to Medallist	20	0	0
Dividends	20	0	0	Balance carried to Balance Sheet	26	12	9
	£46	12	9		£46	12	9

Audited and found correct,

ROBERT S. WHIPPLE, *Honorary Treasurer.*

January 27th, 1926.

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

ELECTION OF OFFICERS AND COUNCIL.

The following Officers and Members of Council were elected for the year 1926-1927 :—

President.—Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President).—Sir Oliver J. Lodge, D.Sc., F.R.S. ; Sir Richard Glazebrook, K.C.B., D.Sc., F.R.S. ; C. Chree, Sc.D., LL.D., F.R.S. ; Prof. H. L. Callendar, M.A., LL.D., F.R.S. ; Sir Arthur Schuster, Ph.D., Sc.D., F.R.S. ; Sir J. J. Thomson, O.M., D.Sc., F.R.S. ; Prof. C. Vernon Boys, F.R.S. ; Prof. C. H. Lees, D.Sc., F.R.S. ; Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S. ; Alexander Russell, M.A., D.Sc., F.R.S. ; F. E. Smith, C.B.E., F.R.S.

Vice-Presidents.—E. H. Rayner, M.A., Sc.D. ; J. H. Vincent, D.Sc., M.A. ; D. Owen, B.A., D.Sc. ; Prof. F. L. Hopwood, D.Sc.

Hon. Secretaries.—Prof. A. O. Rankine, O.B.E., D.Sc., Imperial College of Science and Technology ; J, Guild, A.R.C.S., D.I.C., National Physical Laboratory, Teddington, Middlesex.

Hon. Foreign Secretary.—Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.

Hon. Treasurer.—R. S. Whipple, 45, Grosvenor Place, S.W.1.

Hon. Librarian.—J. H. Brinkworth, M.Sc., A.R.C.S., Imperial College of Science and Technology.

Other Members of Council.—R. W. Paul ; Prof. A. M. Tyndall, D.Sc. ; W. S. Tucker, D.Sc. ; A. Ferguson, M.A., D.Sc. ; J. S. G. Thomas, D.Sc. ; D. W. Dye, B.Sc. ; Sir Richard Paget, Bart. ; E. A. Owen, B.A., D.Sc. ; J. Robinson, M.Sc., Ph.D. ; A. B. Wood, D.Sc.

PRESENTATION OF THE DUDDELL MEDAL.

The PRESIDENT, on behalf of the Council, presented the Duddell Memorial Medal to Albert Campbell, B.A.

After repeating the conditions governing the award, the PRESIDENT said that the medallist's name had been known for a quarter of a century to all who are interested in the design of instruments. He had enriched scientific apparatus with many beautiful devices, and knew Duddell intimately. The speaker, looking back on 20 years' acquaintance with Mr. Campbell as a colleague, attributed his success to his wide scientific knowledge, to his manipulative skill, and to his patience. He had always been generous in his appreciation of others' achievements.

Mr. CAMPBELL, after expressing his thanks, said that the design of instruments involves invention rather than discovery. He thought that in addition to the qualifications which the President had mentioned, the inventor or designer should have a high degree of *distractibility*. He should set his face against conventional methods, and be ready to abandon any line of thought upon which he might be engaged for a new one if this should occur to him. "Scientific wool-gathering" was characteristic of Lord Kelvin.

ELECTION OF AN HONORARY FELLOW.

Prof. CHARLES FABRY was elected an Honorary Fellow of the Society.

VOTES OF THANKS.

A vote of thanks to the Hon. Auditors was proposed by Mr. C. R. Darling, seconded by Dr. J. H. Vincent, and carried by acclamation.

A vote of thanks to the retiring Officers and Council was moved by Mr. T. Smith, seconded by Mr. Rollo Appleyard, and carried by acclamation. Particular reference was made to Prof. Rankine's services in organizing the Annual Exhibition of Apparatus, and to the debt which the Society owes to the retiring President.

A vote of thanks to the Governors of the Imperial College of Science was proposed by Dr. D. Owen, seconded by Prof. F. L. Hopwood, and carried by acclamation. Dr. Owen said that some reference had been made to the Society's need for a home of its own, but he felt that it had been made to feel very much at home in the College.

ORDINARY MEETING FOLLOWING THE ANNUAL GENERAL MEETING.

The following Papers were read:—

1. "On the Hyperbola Method for the Measurement of Surface Tension," by A. FERGUSON, M.A., D.Sc., and I. VOGEL, B.Sc.

2. "The Application of Radiography to the Study of Capillarity," by E. A. OWEN, M.A., D.Sc., and A. F. DUFTON, M.A., D.I.C.

A DEMONSTRATION of "The Application of the Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material" was given by J. J. HARTLEY, M.Eng.M.Sc., A.M.I.C.E., and R. H. RINALDI.

February 26, 1926.

The following Papers were read:—

1. "The Effects of Torsion upon the Thermal and Electrical Conductivities of Aluminium, with special reference to Single Crystals," by J. E. CALTHROP, M.A., M.Sc., East London College.

2. "A Study of the Concurrent Variations in the Thermionic and Photo-electric Emission from Platinum and Tungsten with the State of the Surfaces of these Metals," by T. H. HARRISON B.Sc., King's College, London.

DEMONSTRATIONS of Some Phenomena of Surface Tension were given by Mr. EDWIN EDSER and by Mr. CHARLES R. DARLING, F.I.C.

March 12, 1926.

The following Papers were read :—

1. "The Analogy between Ripples and Acoustical Wave Phenomena," by A. H. DAVIS, D.Sc.

2. "On the Evaporative Losses of Vacuum-Jacketed Metal Vessels of the Dewar Type," by R. M. ARCHER, A.R.C.Sc., B.Sc., M.I.E.E.

The first of the above Papers was illustrated by a Demonstration.

March 26, 1926.

The PRESIDENT announced that the Council had passed the following resolution with regard to the death of Mr. W. R. Cooper, and that three officers of the Society had been able to attend Mr. Cooper's funeral.

RESOLUTION.

> By the death of Mr. W. R. Cooper the Physical Society of London has lost one of its devoted friends, and the Council wishes to express to Mrs. Cooper and family its deep sympathy in their loss.
>
> Mr. Cooper acted as a Member of the Council from February 8, 1901, until February, 1903, when he became one of the Secretaries of the Society. He continued in this office until February 12, 1915, when he was elected a Vice-President. He resigned this position in February, 1918, to accept the responsibilities of Treasurer, and acted in this capacity until his breakdown in October, 1924. He was thus continuously in office for more than 23 years.
>
> It was largely due to his efforts, in conjunction with the late Mr. W. Duddell, that the "Proceedings" were published separately from the "Philosophical Magazine." By taking this step the Society was enabled to publish its Papers more efficiently and with considerable financial advantage.
>
> He was a most careful Treasurer, and the Society is largely indebted for its present financial position to his devotion.
>
> The Council will much miss his good judgment, and the Fellows his lovable personality.

Mr. F. E. SMITH moved that the meeting should associate itself with the Council's resolution. The Fellows present signified their assent by standing.

The following Papers were read :—

1. "Obliquity Corrections in Radium Estimation," by I. BACKHURST, M.Sc.

2. "The Viscosity of Water at Low Rates of Flow, determined comparatively by a Method of Thermal Convection," by Prof. A. GRIFFITHS, D.Sc., A.R.C.S., and P. C. VINCENT, B.Sc., Birkbeck College.

A DEMONSTRATION of some Simple Experiments with Thermionic Valves was given by E. H. RAYNER, M.A., Sc.D.

April 23, 1926.

The Eleventh Guthrie Lecture was delivered by Prof. CHARLES FABRY, who took as his subject "The Absorption of Radiation by the Upper Atmosphere."

A vote of thanks, proposed by Sir ARTHUR SCHUSTER and seconded by Mr. J. H. JEANS, was carried by acclamation.

May 14, 1926.

The following Papers were read :—

1. "The Properties of Mutual Inductance Standards at Telephonic Frequencies," by L. HARTSHORN, A.R.C.S., B.Sc., D.I.C.

2. "A Note on λ 4722 of Bismuth and the Nature of '*raies ultimes,*'" by Prof. A. L. NARAYAN, and K. R. RAO.

3. "The Distribution of Intensity in a Positive Ray Spectral Line," by M. C. JOHNSON, M.A., M.Sc.

A DEMONSTRATION of "Some Experiments with Selenium Cells" was given by Dr. E. E. FOURNIER D'ALBE.

May 28, 1926.

The following Papers were read :—

1. "Static and Isotropic Gravitational Fields," by G. TEMPLE, Ph.D.

2. "On The Diffraction of Light by Spherical Obstacles," by Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN.

3. "On the Absorption and Series Spectra of Nickel," by Prof. A. L. Narayan. and K. R. Rao.

4. "The Influence of Electrolytes in Electro-Endosmosis," by H. C. Hepburn, B.Sc.

June 11, 1926.

The following Papers were read :—

1. "The Latent Heat of Fusion of Some Metals," by J. H. Awbery, B.Sc., and Ezer Griffiths, D.Sc.

2. "The Piezo-Electric Quartz Resonator and its Equivalent Electric Circuit," by D. W. Dye, B.Sc.

3. "The Characteristics of Electrostatic Machines on Non-Inductive Loads and on the Coolidge Tube," by E. J. Evans.

June 25, 1926.

The following Papers were read :—

1. "The Refraction and Dispersion of Gaseous Carbon Disulphide," by H. Lowery, M.Sc.

2. "On the Use of Invar Steel for Precision Balances," by J. J. Manley, M.A.

3. "On the Scattering Power of Oxygen and Iron for X-Rays," by A. A. Claassen.

JAN 2 1926

THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 38.—PART 1.

DECEMBER 15, 1925.

Price to Non-Fellows **6s.** *net, post free* **6/3.**

Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
FLEETWAY PRESS, LTD.,
3-9, DANE STREET, HIGH HOLBORN, W.C.1.
1925.

THE PHYSICAL SOCIETY OF LONDON.

1925-26.

OFFICERS AND COUNCIL.

President.

F. E. SMITH, C.B.E., F.R.S.

Vice-Presidents.

(Who have filled the Office of President)

SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, M.A., LL.D., F.R.S.
SIR ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. VERNON BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E., M.A., F.R.S.
ALEXANDER RUSSELL, M.A., D.Sc., F.R.S.

Vice-Presidents.

C. R. DARLING, F.I.C.
D. OWEN, B.A., D.Sc.
E. H. RAYNER, M.A., Sc.D.
J. H. VINCENT, D.Sc., M.A.

Secretaries.

PROF. A. O. RANKINE, D.Sc.
Imperial College of Science and Technology, South Kensington, S.W.7.

J. GUILD, A.R.C.Sc., D.I.C., F.Inst.P.
Lalbagh, Park Road, Teddington, Middlesex.

Foreign Secretary.

SIR ARTHUR SCHUSTER, Ph.D., Sc.D., F.R.S.

Treasurer.

R. S. WHIPPLE.
45, *Grosvenor Place, London, S.W.*1.

Librarian.

J. H. BRINKWORTH, B.Sc.
Imperial College of Science and Technology.

Other Members of Council.

G. B. BRYAN, D.Sc.
D. W. DYE, B.Sc.
A. FERGUSON, M.A., D.Sc.
F. L. HOPWOOD, D.Sc.
E. A. OWEN, B.A., D.Sc.
R. W. PAUL.
J. ROBINSON, M.Sc., Ph.D.
J. S. G. THOMAS, D.Sc.
W. S. TUCKER, D.Sc.
PROF. A. M. TYNDALL, D.Sc.

Assistant Secretary (Publications).

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley, N.*3.

I.—THE INFLUENCE OF STRAIN ON THE THOMSON EFFECT.

By HUGH E. SMITH, *B.Sc.*, Research Student at Birkbeck College.

ABSTRACT.

The influence of tension on the Thomson effect in wires has been investigated by Nettleton's method. For pianoforte steel, charcoal iron, constantan and nickel, the Thomson coefficient numerically decreases with tension until the elastic limit is reached, after which it increases. With removal and restoration of tension a new definite cycle is followed. The Thomson effect in tungsten, here measured for the first time, increases with tension and also follows a cycle. No change in the Thomson effect is noticed in brass or German silver. Heterogeneity was not present in the specimens investigated.

INTRODUCTION.

CONSIDERABLE attention has been given of late to the effect of strain and torque on the thermal and electrical conductivities of metals, and in May, 1923, Dr. H. R. Nettleton—under whose guidance this research has been carried out—suggested to the writer the probability that strain and torque would cause an alteration in the value of the Thomson effect. Accordingly preliminary experiments were made in the summer of 1923 by reversing the heating current in a wire of constantan passing through two copper blocks and thereby observing the relative deflections on a sensitive galvanometer due to the change in resistance of two detecting coils situated respectively at the quarter and three-quarter positions between the isothermal copper ends and connected to adjacent arms of a Wheatstone Bridge. Such changes in temperature are proportional to the Thomson effect divided by the thermal conductivity of the wire. The experiments were of value in showing in the first place that as the effects of tension and torque on σ/k were very small, the absolute method of measuring σ would have to be pushed to the extreme limits of sensitivity; in the second place that exceptional care would have to be taken in the fixing of the wire through its ends. In view of the difficulty of the work—all measurements having to be taken between 10 p.m. and 7 a.m.—it was found advisable to limit the work to the effect of tension at one temperature only.

METHOD AND APPARATUS.

The method of measuring the Thomson effect is that fully described by Nettleton,* and recently used by Young.† Nettleton has shown that if a wire of sufficiently small length be fixed between isothermal-equipotential ends maintained at temperatures θ_1 and θ_2 respectively and transversed by a current C_1, it is possible to reverse and raise the current to a value C_2 without producing any change in the temperature of the wire. Under such conditions, with justifiable accuracy

$$\sigma=R(C_2-C_1)/J(\theta_2-\theta_1),$$

where

σ=Thomson effect at a temperature $(\theta_2-\theta_1)/2$,

J=number of joules equivalent to one calorie,

R=actual resistance of the wire.

R and C_2-C_1 may be measured with great accuracy.

---

* Proc. Phys. Soc., Vol. 29, p. 16 (1916), and Vol. 34, p. 77 (1922).

† Proc. Phys. Soc., Vol. 37, p. 145 (1925).

Though this method together with its circuit has been adhered to, considerable modifications have been found to be necessary in the actual apparatus used in view of the fact that tension has to be applied; such modifications are described below.

The isothermal-equipotential ends each consisted of two similar blocks of copper (*P* and *Q*, Fig. 1), having a hole *A* bored in the plane of section *XX* of slightly less diameter than that of the wire it was to take. Parallel and close to this hole were larger bores *B*, which could be connected to one another by means of external copper pipes for steam or water heating. There was also a third hole *C* for the potential lead, which could be clamped by means of a copper screw, and a terminal *D* for the heating current. The two sections *P* and *Q* were clamped together by four screws and bolts, thus squeezing the experimental wire tightly in its hole *A*.

Tests were made to show whether these ends were truly isothermal. Currents up to 5 amperes were run for some time in a dummy wire fixed between them and the thermal electromotive force across the ends balanced on a bridge. The current was then switched off and the fact that no change in the balance occurred showed that any heating at the ends was at once entirely dissipated. In this work the heating current run in obtaining the value of $C_2 - C_1$ was only 2 amperes and 1·0183 amperes for the determination of *R*.

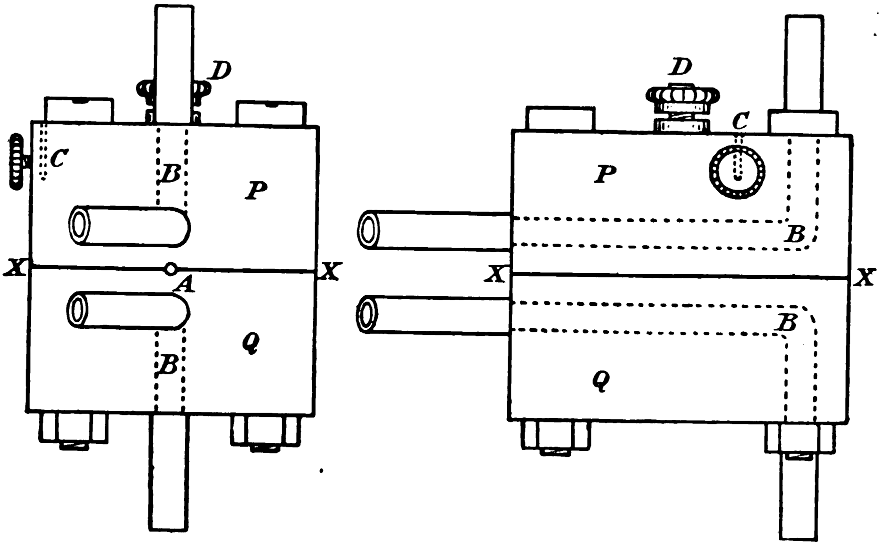


Fig. 1.

The wire—one end of which was fixed—was capable of being placed under tension by means of a differential screw with a 200 lb. spring balance attached to the other end (*see* Fig. 2). A movable platform on rollers supported the heavy copper ends, thus preventing them from bending the wire. The detecting coil, of rather more than one-third the length of the operative part of the wire, consisted of two layers of non-inductively wound silk-covered copper S.W.G.44, which was coated with an insulating enamel to prevent displacement. To prevent any progressive zero shift of the galvanometer spot, due to the warming up of the two layers of wound wool and cotton-wool surrounding the wire and coil, an external compensating coil, suitably thermally lagged, was used; in later work, however, the best device was found to be a coil of a single turn wound directly upon one end of the detecting coil, with their leads brought out side by side, embedded in cotton-wool. The external compensating coil could be used in conjunction with this, but experience showed it to be unnecessary.

Until the later experimental stage large capacity accumulators were not available, accordingly an arrangement was adopted whereby the constant heating current was taken from the 100 volt mains *E*. (The circuit is shown in the upper part of Fig. 2.) Low capacity accumulators *e* were placed in a parallel loop of negligible resistance (r_1 say) to give a slight current which rose or fell as the mains correspondingly fluctuated, thus maintaining a constant potential difference across

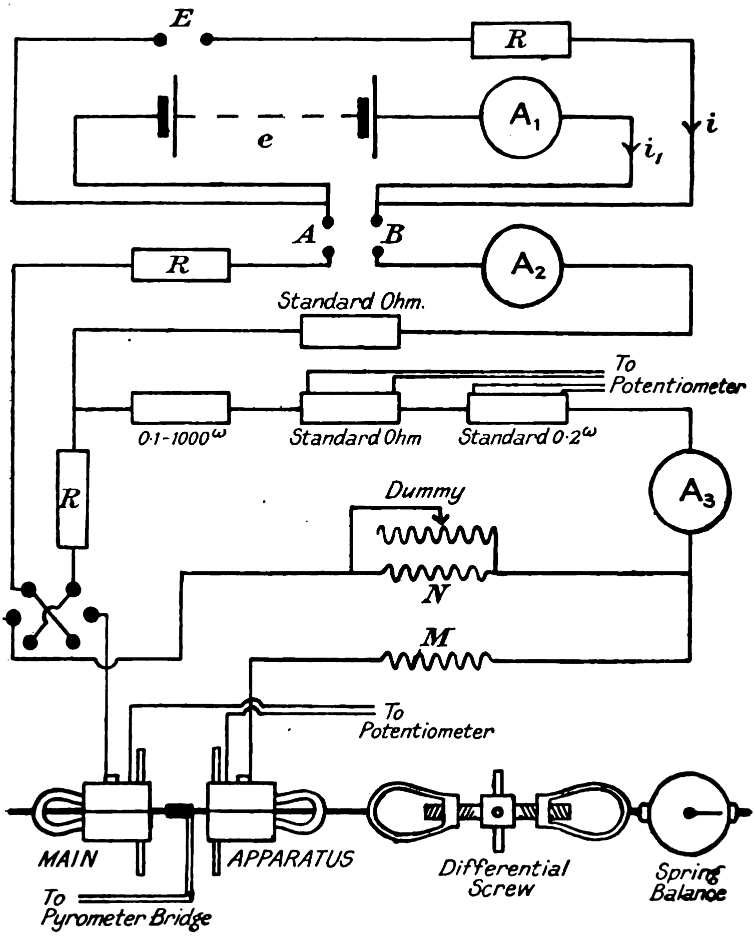


Fig. 2.—*R*, Rheostats. A_1 A_3, Milliammeters. A_2, Ammeter. *M*, *N*, Ohm Resistances.

$A\,B$, and causing a steady current to flow through the main circuit of resistance x say. Applying Kirchoff's Laws we obtain

$$\begin{aligned} C &= (e+Er_1/R)/(r_1+x+r_1x/R) \\ &= e/x \text{ approximately, since } r_1 \text{ is small.} \end{aligned}$$

Also by assuming likely variations of the mains E it may readily be seen that the current in $A\,B$ remains very nearly constant even when r_1 is fully taken into account, providing, of course, it is very small. This arrangement in use was found to be quite satisfactory when a steady constant current was required for long periods of time.

HETEROGENEITY.

The necessity for interchanging the heaters in measuring the Thomson effect was first noted by Le Roux,* who attempted to show that the mean value obtained was the true measure of the Thomson coefficient.

Young† has recently found that in the case of carbon steels a considerable systematically different value of the Thomson effect is obtained by the interchange, which he has shown to be due to the Peltier effect produced inside the wire consequent upon its asymmetrical structure.

When this work was first commenced the result of interchanging the heaters was invariably investigated, but as no effect was found the writer grew to ignore its probability. On learning that Young was encountering this effect, the writer made very careful studies and it was found that less than ½ per cent. difference occurred, save in one piece of the steel wired used. This difference, which is here given, disappeared on strain (Table I). It might be added that this particular piece was the end and last of that particular specimen of steel wire, which fact seems to be in accordance with the experience of Young.

TABLE I.—*Heterogeneous Steel Specimen.*

Tension $\times 10^9$ Dynes/cm.^{2}	Heater Hot.	θ_2	θ_1	$\theta_2-\theta_1$	C_2-C_1 in amps.	R in ohms.	$\sigma_{55\cdot5}\times10^{-6}$ Calories/coul.-deg.
0 (virgin)	A	99·99	11·40	88·59	0·08060	0·009765	$-2{\cdot}12_5$
	B	99·98	11·55	88·43	0·06160	0·009767	$-1{\cdot}62_8$
12	A	99·98	11·58	88·40	0·06157	0·009809	$-1{\cdot}63_8$
	B	99·98	11·58	88·40	0·06160	0·009809	$-1{\cdot}63_9$
0	A	99·69	11·90	87·79	0·06114	0·009791	$-1{\cdot}61_5$
	B	99·69	11·20	88·49	0·06111	0·009786	$-1{\cdot}60_1$

It is worthy of note, however, that whilst Young experienced a change when the wire was under the temperature gradient of its heating current—the ends being at the same temperature—the writer has not found this to occur. (The heterogeneous specimen mentioned above was not tested in this way before strain.) On occasions, when a new wire has been put in the ends to replace an old one for testing purposes without first obtaining a fresh surface of contact in the ends, it has been found to yield inaccurate results. This was put down to the fact that a film of oxide due to the heat had occurred at the points of contact of the isothermal ends and the wire.

---

* Ann. de Chimie et de Phys., Vol. 10, p. 258 (1867).

† Loc. cit.

This is only one case in point, but it was also found that unless exceptional care was taken, inconsistent results were easily obtainable as a result of bad ends. Thus it seems possible that heterogeneity, real and pseudo, may easily occur.

In all the results given below heterogeneity was absent in the specimens within the limit given—i.e., a half per cent. This is of extreme importance, as in the steel result given below (Fig. 3) the greatest change in the Thomson coefficient, due to a difference of 200 lb. tension on the 18-gauge wire, is only about 4½ per cent., whereas heterogeneity was experienced by Young in steel at this temperature, causing up to 50 per cent. change in the Thomson effect. In fact, the largest percentage change observed, which was in tungsten, was only about eight, for the maximum tension applicable.

RESULTS.

The work was handicapped in connexion with certain metals, notably constantan and nickel, which commenced to flow under high tension, the wire slipping in the ends after a certain tension had been reached, and thus preventing further readings being taken. Slip could at once be detected by the accelerated rise in the resistance, which still further increased when the tension was removed.

Measurements were carried out for pianoforte steel, charcoal iron, constantan, nickel, tungsten, German silver and brass. The operative lengths of the wires were from 4 to 5 cm., according to their thermal conductivities. The results for those metals which showed a change in the Thomson effect are given in graphs with σ plotted against the tension, and tables are given of those which remained constant.

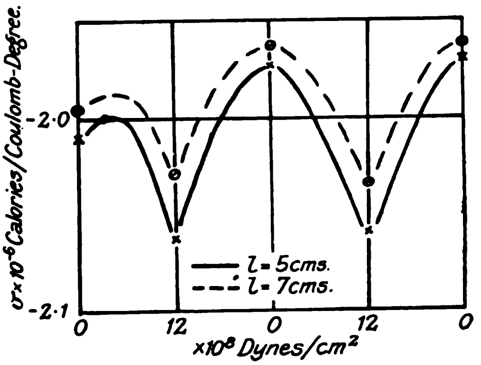


FIG. 3.—PIANOFORTE STEEL.

An example is given in the case of steel (Fig. 3) showing the effect of increasing the operative length of the wire in an attempt to gain sensitivity. It will be seen that an increase of 2 cm. on 5 cm. at once invalidates the assumption that emission losses are negligible.

It will be noticed from the graphs of steel, iron and constantan that a virgin or unstrained wire gives quite different results from one which has already been subjected to tension. In these virgin wires the Thomson effect NUMERICALLY decreases with tension until the elastic limit is reached, at which point it then increases. After a maximum strain has been reached, it then follows a definite cycle with the tension, decreasing as the tension is lessened, and increasing as the tension is restored. Several cycles were made, and were found to be quite definite. Nickel also behaves in a

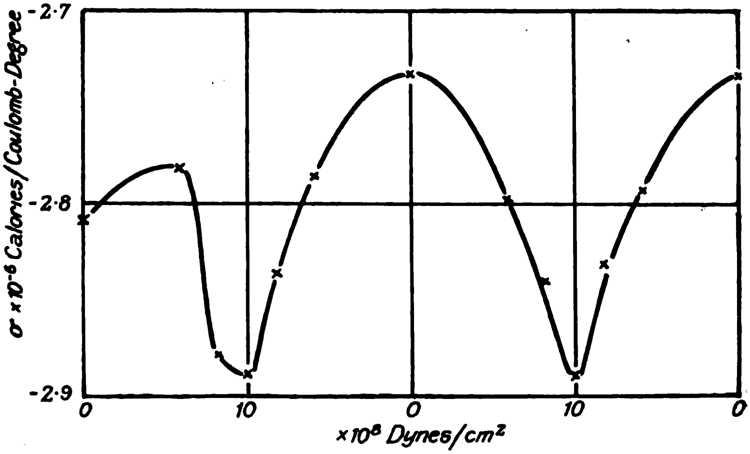


FIG. 4.—CHARCOAL IRON.

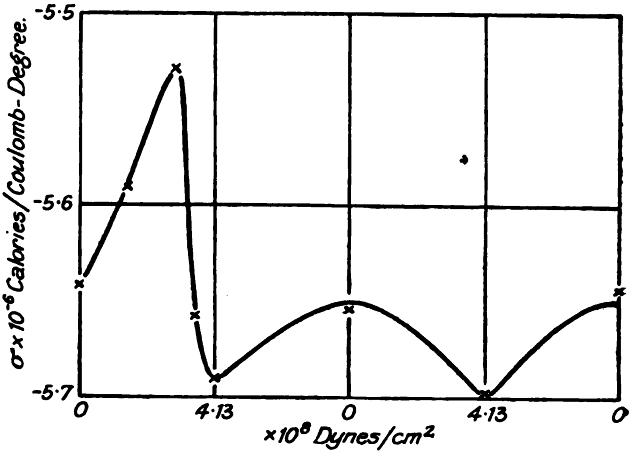


FIG. 5.—CONSTANTAN.

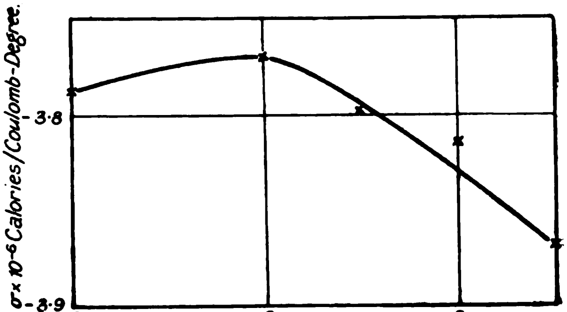


FIG. 6.—NICKEL.

like manner, but unfortunately cycles could not be proceeded with owing to the wire flowing and thus slipping in the ends, as has been mentioned above.

The Thomson effect in tungsten has never previously been measured, except at incandescent temperatures. For this reason a short table, as well as a graph, is given here (Table II). The specimen was 99·95 per cent. purity; the impurities being Fe 0·014 per cent., Mn 0·010 per cent., Ca 0·007 per cent., Ni 0·0052 per cent., with a trace of silicon. This was the only metal of positive Thomson coefficient investigated; and, due to the limitation of the tension apparatus available, it was impossible to exceed the elastic limit. However, the metal behaved in a similar manner to those given above, the Thomson coefficient increasing with tension and following a definite cycle on removal and restoration of the strain.

TABLE II.—*Tungsten.*

Tension $\times 10^9$ dynes/cm.^{2}	θ_2	θ_1	$\theta_2-\theta_1$	C_2-C_1 in amps.	R in ohms.	θ	$\sigma_\theta \times 10^{-6}$ Calories/coul.-deg.
0 (virgin)	99·49	11·90	87·59	0·24156	0·003089	55·7	$+2{\cdot}03_8$
2·95	99·47	11·92	87·55	0·24618	0·003090	55·7	$+2{\cdot}07_9$
5·90	99·47	11·98	87·49	0·24905	0·003091	55·7	$+2{\cdot}10_5$
8·85	99·47	11·98	87·49	0·25493	0·003103	55·7	$+2{\cdot}16_2$
11·80	99·47	12·08	87·39	0·26022	0·003119	55·8	$+2{\cdot}22_2$
0	99·47	12·12	87·35	0·26024	0·003[illegible]89	55·8	$+2{\cdot}20_1$

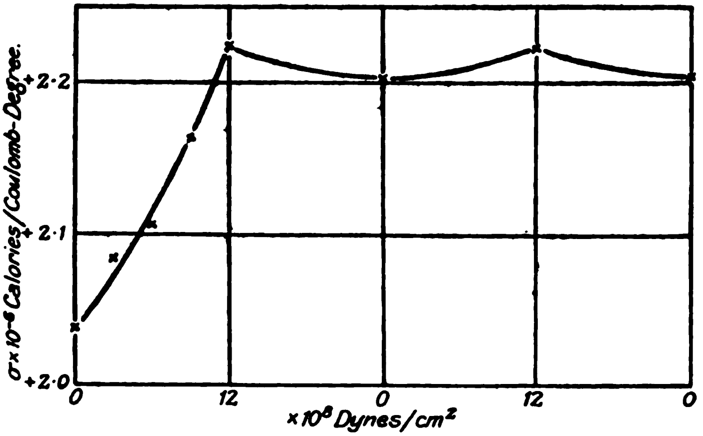


FIG. 7.—TUNGSTEN.

TABLE III.—*German Silver.*

Tension $\times 10^9$ dynes/cm.^{2}	θ_2	θ_1	$\theta_2-\theta_1$	C_2-C_1 in amps.	R in ohms.	0	$\sigma_\theta \times 10^{\;6}$ Calories/coul.-deg.
0 (virgin)	100·22	9·50	90·72	0·1286	0·008454	54·8	$-2{\cdot}86_6$
2·95	100·21	9·44	90·77	0·1287	0·008465	54·8	$-2{\cdot}87_0$
5·90	100·20	9·50	90·70	0·1278	0·008485	54·8	$-2{\cdot}86_0$
8·85	100·20	9·52	90·68	0·1277	0·008515	54·8	$-2{\cdot}86_8$
10·62	100·19	9·52	90·67	0·1272	0·008554	54·8	$-2{\cdot}87_0$
0	100·19	9·49	90·70	0·1288	0·008445	54·8	$-2{\cdot}86_9$

TABLE IV.—*Brass.*

Tension $\times 10^9$ dynes/cm.^{2}	θ_2	θ_1	$\theta_2-\theta_1$	C_2-C_1 in amps.	R in ohms.	θ	$\sigma_\theta \times 10^{-6}$ Calories/coul.-deg.
0 (virgin)	99·40	13·50	85·90	0·02885	0·003435	56·5	$-0{\cdot}276_0$
2·95	99·40	13·50	85·90	0·02882	0·003440	56·5	$-0{\cdot}276_1$
5·90	99·40	13·50	85·90	0·02868	0·003458	56·5	$-0{\cdot}276_2$
8.85	99·40	13·50	85·90	0·02831	0·003497	56·5	$-0{\cdot}275_7$
10·03	99·40	13·50	85·90	0·02806	0·003525	56·5	$-0{\cdot}275_4$
0	99·40	13·50	85·90	0·02874	0·003452	56·5	$-0{\cdot}276_3$

Any changes which may have occurred in the Thomson coefficient in German silver and brass on the application of strain were very small and within the limit of experimental error.

In conclusion, the writer wishes to take this opportunity of expressing his gratitude to Dr. Nettleton for his great assistance and advice, and of recording his thanks to Prof. A. Griffiths, Head of the Physical Dept., Birkbeck College, for placing so much apparatus and room at his disposal for such a length of time.

DISCUSSION.

Prof. A. GRIFFITHS said that the Paper afforded a good example of what could be achieved by an evening student in particularly difficult circumstances. The author had unfortunately been compelled, while his work was in progress, to take up a post which obliged him to live in Lincolnshire, so that it had been necessary for him to travel to London night by night in order to carry out his experiments. It might be added that the acknowledgment of Dr. Nettleton's assistance was not to be understood as a formal one, for Dr. Nettleton had generously accommodated himself to the unusual conditions under which the work had been carried out, whenever his advice and help had been required.

Mr. W. A. BENTON asked whether he correctly understood the author to say that the cyclic repetitions shown by his curves applied only to specimens which had been strained beyond the elastic limit. If so, the result is a very surprising one. When a specimen has been stressed it recovers all its ordinary physical properties when the stress is removed, unless the elastic limit has been exceeded: is it to be understood that the Thomson coefficient follows quite the opposite rule? And has the author made any repeating cycles of observations for strains lying well within the elastic limit?

Mr. R. S. WHIPPLE said that the same question had occurred to him, and he would like to suggest that the author should try whether the Thomson coefficient was affected by annealing a wire which had been strained. It is easy to free a wire from all strain by this process, and quite a moderate annealing temperature will serve, a change of 50°C. being sufficient. It might be worth while, therefore, to take observations before and after annealing a specimen.

Mr. J. GUILD said that as the author had asked for suggestions, he would like to make two. (1) Possibly the difficulty which had been experienced with regard to the slipping of the specimens in the clamps could be got over by using very strong spring washers tightened up as much as possible. (2) Very fine enamelled wire can be obtained, and as this takes up much less space than double-silk covered wires and is otherwise satisfactory, it might be more suitable for the construction of the detecting coil.

Mr. F. E. SMITH said that as he disliked using thermo-couples himself, he would suggest to the author the possibility of substituting a resistance method of finding the temperature of a specimen. For this purpose it might be desirable to employ a modification of the Kelvin bridge in which, besides the extra mesh ordinarily added at the end of one of the galvanometer leads, a further mesh is added at the end of one of the battery leads. He congratulated the author on having carried through so much work under such trying conditions, and expressed particular interest in the arrangement shown in Fig. 2 for obtaining a steady current from the mains.

Mr. JAMES YOUNG (communicated): I should like to express my appreciation of the careful piece of work which Mr. H. E. Smith has carried out on the influence of strain on the Thomson effect. I had the pleasure, some time ago, of seeing his apparatus, and I fully realise the difficult conditions under which he had to work and which he seems to have combated successfully by experimenting during the night. His remarks under the heading "heterogeneity" are of interest to me. I notice (Table I.) that he has detected an asymmetry of 27 per cent. in a specimen of steel wire, but unfortunately has not given the percentage composition of the steel. This is important because asymmetry, if it occurs, only becomes marked when the percentage of carbon in the steel exceeds a certain value (at least 0·6 per cent.). There seem to be two types of asymmetry in wires, which exhibit themselves in Thomson-effect measurements. One of these occurs only when the wire is under the temperature gradient due to the heaters; the other can be detected even if the temperature gradient is due to the current in the wire alone. It was the latter of these phenomena which I attempted to explain in my recent Paper on the Thomson effect, to which Mr. Smith refers. I have been unable to give any satisfactory explanation of the former phenomenon, which when present is generally small (about 5 per cent. in iron). The changes due to strain which Mr. Smith has detected in charcoal iron are of this order of magnitude and perhaps some explanation of this type of asymmetry in terms of strains could be given.

AUTHOR'S reply: In reply to Mr. Benton and Mr. Whipple, the cycles were made after maximum tension had been applied—that is, after the elastic limit had been exceeded. With some specimens the cycles were repeated after the interval of some days, and the values previously obtained were again recorded. This does not apply to tungsten, where all measurements were made with stresses within the elastic limit; but here again σ followed a cycle with removal and restoration of tension. This cycle was not repeated after several days. I must express my thanks for the suggestions given.

(Communicated subsequently): The suggestions that cycles be made for strains lying well within the elastic limit and the annealing of wires were considered, but had not been carried out owing to pressure of time, and also in the latter case owing to the fact that an annealed wire tends to flow more readily than an unannealed wire under high tension. I agree that experiments conducted on these lines would be of value as an addition to those in the Paper. I thank Mr. F. E. Smith for his suggestion of using a Kelvin bridge in place of the thermo-electric potentiometer. I would like to point out the following:—

1. The T.E. potentiometer allows R and C_2-C_1 to be measured under the temperature gradient with great rapidity and an accuracy greater than is required.
2. The value of the standard ohm is eliminated by using the T.E. potentiometer for R and C_2-C_1.
3. The Kelvin bridge requires additional space and apparatus.
4. Thermo-couples were not employed in this work, though they were used in the other Papers referred to in this Paper.

I greatly appreciate Mr. J. Young's remarks, but as only one specimen of the steel wire exhibited any measurable heterogeneity—which disappeared under tension—I can add no further remarks of value, as much further work is necessary in order to investigate any heterogeneity which may appear. I regret that the percentage composition of that heterogeneous specimen of steel has not been determined. It was ordinary commercial "pianoforte steel" wire.

II.—ON THE FLASHING OF CERTAIN TYPES OF ARGON-NITROGEN DISCHARGE TUBES.

By William Clarkson, *M.Sc.*, *A.Inst.P.*, Armstrong College, Newcastle-on-Tyne.

Received July 10, 1925.

Abstract.

The Paper gives an account of investigations on the flashing of discharge tubes* having various types of electrodes, and in which the filling gas, a mixture of argon and nitrogen, had a wide pressure range.

It is shown that the observations are in general agreement with those obtained previously on neon† and air‡ discharge tubes, minor differences between tubes being discussed, and that at higher pressures the discharge was no longer of the "glow" type, but took place between definite points on the electrodes.

Introduction.

THE following Paper is a continuation of previous work on the flashing phenomena of discharge tubes, in which, as the electrodes are only one or two mms. apart, the positive column is absent, and only the negative glow, with an occasional anode glow, is in evidence.

The initial experiments of flashing were confined to "Osglim" lamps, but later air discharge tubes were constructed. In the "Osglim" lamps the electrodes were of iron, and the filling gas, a mixture of neon and helium, in all cases was at approximately the same pressure, that giving the lowest sparking potential. By employing air as a filling gas, however, it was possible to vary the type of tube and the pressure of the gas at will, though actually most of the experiments were performed on converted "Osglim" lamps and on tubes having parallel molybdenum wires as electrodes, and as the critical potential for air is high, lack of suitable capacities limited the pressure range for all but small capacities to about 4 mms.

Since as much general information as possible on flashing was required, it was considered desirable to extend the investigations to more varied types of discharge tubes and over a wide range of pressures. It was essential to obtain, therefore, first of all a supply of gas giving low critical voltages. The critical potential conditions were found to be satisfied by the argon-nitrogen mixture contained in "Osram" gas-filled lamps, and a plentiful supply of this gas was made available through the generosity of the G.E.C., who provided a number of lamps whose filaments had broken.

In order to make apparent any peculiarities due to one tube, or to the material and shape of its electrodes, tubes of the following types were employed: "Osglim" lamps of both the beehive and letter patterns, tubes in which the electrodes were parallel wires, and tubes having for one electrode a helix of wire and for the other a straight wire down the axis of the coil. The wires were of iron, copper, aluminium or molybdenum. In mounting, the electrodes were fixed as far from the containing vessels' walls as possible, this not only enabling the tube to become heated with safety, but also diminishing wall effects.

---

* *See* Pearson and Anson, Proc. Phys. Soc., Vol. 34, p. 204.

† Taylor and Clarkson, Journ. Sci. Insts., Vol. 1, p. 173; also Proc. Phys. Soc., Vol. 36, pt. 4, p. 269.

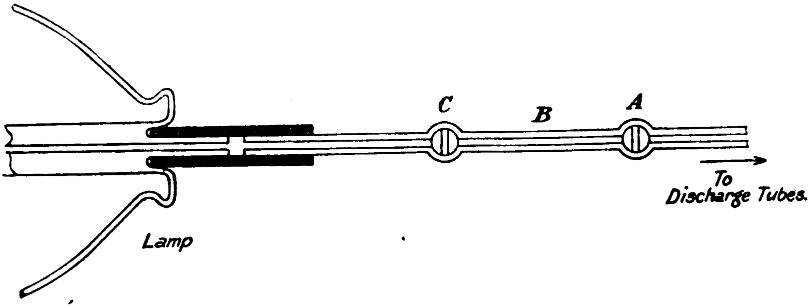
‡ Taylor and Clarkson, Proc. Phys. Soc., Vol. 37, pt. 3, p. 130; also Phil. Mag., Vol. 49, p. 336.

For the measurements of the apparent upper and lower critical voltages V_C and V_B of the tubes under conditions of continuous flashing, a new method described by Taylor and Sayce* was utilised. This method is based upon the ordinary peak voltage measurer, a valve being utilised to ensure unidirectional conductivity from a condenser which becomes charged either to the upper or lower critical voltages, as desired, when connected in parallel with the discharge tube and charging condenser.

GAS APPARATUS.

A description of the method by which the gas was transferred from the lamp bulb to the apparatus may prove of interest here. Nippleless bulbs were utilised, these having a filling tube projecting into the cap at the base.

The cap being removed, the filling tube was connected to the apparatus by means of a short length of pressure tubing, and the taps *A* and *C* being opened, the apparatus, was evacuated to its lowest limit, the connexion then being treated with sealing wax till no leaks were apparent. The tap *C* was then closed, and the tip of the filling tube was smashed with pliers through the pressure tubing connection, the sealing wax previously having been softened at this point. A coating of shellac completed the joints.



It appeared, however, that all precautions were unable to prevent a gradual leakage of air into the gas, though this was always so slight that the critical constants never varied greatly during the life of one bulb, one 200-watt lamp ensuring a supply of gas of suitable properties sufficient to fill the apparatus several times.

The gas-filling apparatus was manipulated in the usual way, the tap *C* serving to admit the relatively high-pressure gas from the bulb to the exhausted space *B*, which gas, when *C* was closed, finally was allowed to enter the discharge tube through the tap *A*.

The discharge tubes at first were "flushed out" thoroughly with the gas, and afterwards were always filled to the highest pressure desired, no additions of gas being made during any series of observations. Phosphorus pentoxide drying tubes were used.

---

* Not yet published.

PREPARATION OF TUBES.

The method employed in the preparation of the discharge tubes was essentially the same as that described in previous work,* similar difficulties being encountered. A tube was considered suitable when the apparently inevitable changes in the critical voltages with time and with continued use were negligible, and when, on altering the circuit, the apparent critical voltages showed no appreciable "lag" behind their final values. All tubes, however, could not be made to fulfil these conditions, even when overrunning at red heat was resorted to, and many finally had to be rejected.

EXPERIMENTAL RELATIONS.

Flashing was observed over a series of pressures ranging from 0·2 mms. to 45·0 mms., these being the limits imposed by the voltages and the resistances available. At pressures lower than some 2·0 cms. the flash was of the normal type, a glow discharge, but at the higher pressures the discharge was of the nature of an "arc," and the negative glow was rarely in evidence.

The relations given below are for the normal discharge; reference is made to the other form later.

CRITICAL VOLTAGE MEASUREMENTS.

Except for the slight unavoidable variations mentioned above, measurements in all tubes showed that for any one tube at a constant pressure the upper and lower critical voltages for steady discharge, v_c and V_b respectively were constants, and that V_C and V_B, the apparent upper and lower critical voltages for conditions for continuous flashing, were also constant, providing the external circuit remained unaltered.

Observations on the effect of the presence of radium on the apparent critical voltages† confirmed the previous result that V_B apparently was unaffected. It was found, however, that V_C invariably was lowered, changes of from 2 to 70 volts being recorded, the magnitude of this change varying with the tube employed. As previously, the tubes least affected were those such as the "Beehive," in which the inter-electrode space was largely screened by the electrodes.

During flashing experiments the radium always was kept at the same place, touching the bulb as near to the electrodes as possible, observations demonstrating that the effect fell off rapidly with the distance of the radium from the tube. It was possible to change V_C at will by varying the distance suitably. In the daylight, when presumably the gas already was partially ionised, no effects were detected when the radium was only 40 or 50 cms. from the tube, but in darkness effects have been noticed with the radium some metres away.

CRITICAL VOLTAGE VARIATIONS.

Observations made on the variation of V and V_B with the charging voltage E, the circuit resistance R, and the capacity C,‡ showed that V_C and V_B, though apparently independent of E and R, and also practically constant for values of C down to about 1·0 microfarads, in general changed rapidly as the capacity was further reduced, though the magnitude of this change and whether an increase or decrease in value occurred seemed to depend on other factors beside the capacity.

---

* Taylor and Clarkson, Phil. Mag., Vol. 49, p. 336.

† Taylor, Clarkson and Stephenson, Journ. Sci. Insts., Vol. 2, No. 5, p. 154. Taylor and Stephenson, Phil. Mag., June (1925).

‡ Taylor and Stephenson, Phil. Mag., June (1925).

The curves showing the variation of V_C and V_B with pressure were of the same general form as those obtained for air, the change in V_B was never as great as that in V_C, and was generally much smaller, in some cases V_B being the same at all pressures.

RELATIONS FOR TIME OF FLASH (T).

In all, flashes ranging in frequency from many thousands per second to one flash in two minutes were obtained, but in examining flashing relations only those frequencies which could be measured by a stop watch method were considered, the rate of flash varying in practice from about seven flashes per second to about one flash in twenty seconds, for even at this slow rate flashing was still quite regular. Only when the rate of flashing reached the order of one flash in some sixty seconds did irregularities occur, this, of course, being easily explained when account is taken of the effects of quite small fluctuations in E and V_C, and of the inevitable leakage in circuit.

In all cases, from the graphed relations it was found that the relation between T and C was linear if E and R were constant, the same relation holding between T and R when E and C were constant, the linearity being satisfied to a high degree of accuracy and the curves intersecting the axes at points near to the origin. This is in accord with the theoretical relation developed during the work on air, given fairly exactly by

$$T = CR \,.\, \log_e \frac{E - V_B}{E - V_C} + \triangle C,$$

where $\triangle$ is a small constant, since the variation in V and V_B over the range of capacities employed was quite small.

RELATIONS FOR THE CRITICAL RESISTANCE R_c.

Though it was found impossible to obtain as complete a series of results for R_c as for the other flashing phenomena, the high conductivity tubes presenting the same difficulties as in air, in all cases where the results were repeatable it was observed that whilst R_c was only slightly affected for changes in the capacity at least for values of C greater than about 1 microfarad it varied linearly with E. The intercept (V_b') on the voltage axis was of the same order as V_B, the relation

$$R_c = \frac{E - V_b'}{\psi(V_b')}$$

being satisfied to a fair degree of approximation.

ELECTRODE FATIGUE AND OTHER EFFECTS.

Though the general behaviour of discharge tubes was found to be the same in all cases and to agree with theory, the critical voltage measurements revealed the occurrence of phenomena which merited further explanation, chief of these being the anomalies in the variation of V_C and V_B with capacity (and, perhaps, pressure). Whilst it was known that wall charges and impurities in the gas could occasion abnormalities, the evidence indicated that the cause of these anomalies lay in the electrodes themselves, in which case probably films of absorbed gas on the cathode were responsible. This same reason would also serve to explain such facts as the following: That tubes often show great reluctance to adopt new values for V_C and V_B, lags of some fifteen minutes being recorded, that the values of these constants for tubes recommencing flashing after a period of disuse differed markedly from those stable values attained a few minutes later, and that even slight over-running often caused radical changes in their values. It was on account of these changes that over-running at red-heat was discontinued save in refractory tubes.

It is obvious from these results that when work of an exhaustive nature is to be undertaken, such effects as these must be taken into account before a tube can be declared suitable for such work.

The normal electrode fatigue did not occasion much trouble, save in R_c experiments, where, of course, its effects were often disastrous. Its presence was effectively demonstrated in tubes carrying a steady discharge which did not utilise the whole of the cathode, the usual state of affairs at R_c. In these cases the discharge often shifted from place to place on the electrodes, these effects being most striking in tubes with "beehives," or helical cathodes, the change being rotary and often occurring with great rapidity.*

Flashing at High Pressures.

As pressures of the order of 1·5 to 2·0 cms. were employed, the flashes grew more and more intense, being accompanied by a ringing of the electrodes, and it was observed in all tubes that violent discharge having the appearance of an arc or spark frequently occurred, this type displacing the glow discharge altogether at still higher pressures. Observations made on this form for very rapid flashing, when, of course, the form of the discharge could be observed distinctly, showed that the discharge actually took place between points, though a small cathode glow might be present.

Measurements showed that the apparent critical voltages were only approximately constant, the discharge even with small capacities apparently causing irregularities in their value by its intense nature. The discharge grew more intense as larger capacities were employed, until finally, when the energy transference was large each flash was in the form of a loud, vivid spark.† When this occurred it was seen that the value of V_B had fallen often entirely to zero, the condenser being completely discharged at each flash, but that V_C appeared to be unaffected.

This violent spark discharge was similar to a discharge occurring spasmodically in some air discharge tubes when salient points were present, it being observed that salient points tended to have the same effect in argon-nitrogen tubes.

The author wishes to acknowledge here his indebtedness to Prof. G. W. Todd, of Armstrong College, under whose supervision the work was carried out.

---

* Taylor, Nature, September 24 (1924).

† J. W. Bispham, Proc. Roy. Soc., A 81 (1908).

DISCUSSION.

Mr. C. C. Paterson said that the gas used in the experiments was a mixture in which the proportion of argon to nitrogen was not very rigid. One lamp might differ considerably from another in this respect.

Dr. D. Owen remarked that the author had omitted to say what were the values of the critical voltages he had measured : he hoped this omission would be remedied.

Mr. F. E. Smith said he was sure the meeting would learn with deep regret that Mr. Anson, who first discovered the flashing of glow lamps, had been killed in an accident during the summer.

Author's reply (communicated) : In reply to Dr. Owen, I would like to add that V_C ranged from 270 volts to 500 volts, the corresponding variation in V_B for normal flashing being of some 190 to 300 volts. The critical voltages had minimum values at pressures of a few millimeters.

Though curves showing the variations of V_c and V_b with the capacity and pressure were plotted in all cases they were omitted from the Paper because it was felt that a description of their general resemblance would suffice, the particular differences depending solely on the tube used, and, as Mr. Patterson suggested, on the argon-nitrogen mixture employed.

III.—ON THE VISCOSITY OF AMMONIA GAS.

By R. S. Edwards, *A.R.C.S., B.Sc., D.I.C.*, and B. Worswick, *A.R.C.S., B.Sc., D.I.C.*

Received September 4, 1925.

Abstract.

The viscosity of ammonia gas has been determined at three different temperatures by transpiring the gas through a capillary tube which had previously been calibrated with air. Sutherland's constant is found to be roughly 370, and the mean collisional area of the ammonia molecule $0{\cdot}633 \times 10^{-15}$ sq. cm.

I. Object of Investigation.

Previously no experiments on the viscosity of ammonia have been carried out over a wide range of temperature, and the object of this investigation was to study the variation of this viscosity with temperature, and to determine Sutherland's constant for the gas.

II. General Method of Procedure.

The method employed was that of transpiration of the gas through a capillary tube, the dimensions of which were ascertained by transpiring air. This method is essentially the same as that followed by Mr. H. Harle in his work on the "Viscosities of the Hydrogen Halides."*

The purified gas was liquified and then enclosed and allowed to evaporate. The process of evaporation could be controlled so as to establish a suitable driving pressure, the pressure difference between the ends of the capillary being measured on a U-tube gauge. The mass of gas passed was measured by the standard alkali-acid process for ammonia. The corresponding volume was obtained from density data.

III. Constant of Capillary Tube.

About twenty tubes of approximately 0·25 mm. diameter were calibrated and the most uniform chosen. That chosen was about 55 cms. long, with mean diameter 0·246 mms., its maximum variation being less than 1 per cent. of the mean diameter. The mean diameter was found by weighing a thread of mercury which occupied the length of the tube.

The type of apparatus used is shown diagrammatically in Fig. 1. Air was drawn through the capillary tube by means of the aspirator *B*, the volume of water collected giving, after several corrections, the volume of air passed. The end *A* of the capillary tube was open to the atmosphere through drying tubes containing calcium chloride, soda lime and glass wool. The spiral S_1 consisted of about 70 cms. of thin walled 4 mm. tubing. S_2 was a small spiral inserted to take up any strains produced in the assembling of the apparatus. The calcium chloride tube *D* was inserted between S_2 and B to prevent moisture from the aspirator reaching back to the capillary tube. The pressure difference was read from the manometer M, which was a mercury gauge with wide arms to eliminate capillary effects. The difference of level was noted by a cathetometer reading to 0·1 of a mm.

---

* Proc. Roy. Soc., A. Vol. 100, p. 429 (1922).

To obtain concordant results it was found necessary to reduce "dead-space" on the aspirator side to a minimum. Further, it was necessary to ensure that the gas remained at a constant temperature after entering the capillary and during its passage to and in the aspirator. To realise these conditions it was found necessary to replace Mr. Harle's large aspirator, which gave a constant head, by a smaller vessel giving a slightly varying head. To maintain a uniform temperature the water from the jacket was circulated round the aspirator and drying tube, as shown in figure. This arrangement was extremely satisfactory. Variations in the pressure head were conveniently made between wide limits by varying the height of a nozzle attached by pressure tubing to the exit tube.

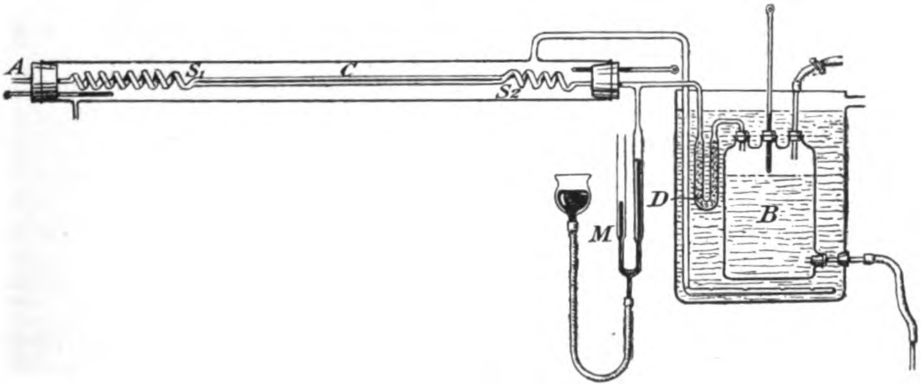


FIG. 1.

Meyer's transpiration formula

$$P_1V_1=P_2V_2=\frac{(P_1^2-P_2^2)\pi a^4}{16\eta l}$$

can be written

$$\eta=\frac{(P_1-P_2)(P_1+P_2)\pi a^4}{16P_2V_2l}=\frac{\delta(2P_1-\delta)\pi a^4 60g\rho_0}{16(P_1-\delta)V_2l}$$

where P_1=atmospheric pressure$=P_2+\delta$.

δ=pressure difference (obtained from gauge readings) measured in cms. of mercury at 0°C.

ρ_0=density of mercury at 0°C.

V_2=volume of dry air passing per minute at pressure P_2 and temperature of jacket t_c°C.

Actually P_2 decreased with the time, and a modified form of Meyer's formula should be used; but, since the variation was never more than 0·1 per cent., the assumption that δ was equal to the mean pressure difference was quite justifiable. The volume of water collected gave the increase in the volume of saturated air in the aspirator at pressure P_2 and temperature t_a (t_a being the temperature of the air in the aspirator). The temperature t_a never differed from t_c by more than 0·1°C.

Since P_2 remains approximately constant, the partial pressure of the air in the aspirator is less than P_2 by the saturation vapour pressure of water at t_a, so that if V=observed volume of water displaced per minute we have

$$V_2=\frac{(P_2-\sigma)V}{P_2}=\frac{(P_1-\sigma-\delta)V}{P_1-\delta}$$

where σ=saturation vapour pressure of water at t.

Substituting in the equation for η we have

$$\eta=\frac{60g\rho_0\pi a^4}{16l}\cdot\frac{\delta(2P_1-\delta)}{(P_1-\delta-\sigma)V}=K\frac{\delta(2P_1-\delta)}{(P_1-\sigma-\delta)V}$$

where K is the constant of the tube.

One further correction is necessary for the value of K thus determined. This correction is for the slipping of the gas over the walls of the capillary tube.

This correction occurs as a factor $\left(1+\frac{4\varphi}{r}\right)$ in the expression for the viscosity where φ is the coefficient of slip. Thus the value of K above must be divided by this factor.

The value of φ was calculated according to the formula given by C. J. Smith,* namely,

$$\varphi=\frac{1\cdot70\,\eta\sqrt{3RT}}{(p_1+p_2)}$$

where p_1 and p_2 are initial and final pressures, T is absolute temperature and η is the viscosity. This correction was of the order of 0·7 per cent.

The values of $\eta_{(\text{air})}$ used in calculating K are the most recent of Prof. Rankine—viz.,

$\eta_0=1\cdot724\times10^{-4}$ C.G.S. units
$\eta_{15}=1\cdot799\times10^{-4}$,, ,,

All joints in the apparatus were, as far as possible, of glass, the others necessary being well sealed with collodion. This gave perfectly airtight joints.

The results were concordant up to a pressure difference of 6·1 cms. of mercury. With differences exceeding this turbulence set in.

The temperature of the jacket and aspirator was maintained constant by passing a rapid stream of water through the circuit. The jacket temperature was taken as the mean of the inlet and outlet temperatures measured with mercurial thermometers graduated to 1/10°C. These and the aspirator thermometer were calibrated by comparison with a standard mercurial thermometer.

The volume of water collected was found by weighing, corrections being applied for buoyancy and density as usual. The times were measured with a stop watch.

---

* Proc. Roy. Soc., A, Vol. 106 (1924).

LIST OF RESULTS FOR *K*.

TABLE I.

t°C.	$K \times 10^5$	t°C.	$K \times 10^5$	t°C.	$K \times 10^5$
12·05	6·52	12·14	6·57	11·00	6·57
12·16	6·57	11·99	6·56	12·82	6·54
11·76	6·54	11·46	6·51	12·28	6·53
11·55	6·56	11·30	6·57	12·78	6·58
11·88	6·57	11·41	6·57	1 ·71	6·57
12·03	6·58	11·58	6·57	13·82	6·57

Mean value of $K=6{\cdot}56\times10^{-5}$.

Mean value of $t=11{\cdot}87$°C.

Correction factor for slipping for air$=1{\cdot}0067$.

The mean value of t is taken because of the small variation of K over our range of temperature.

IV. PREPARATION OF AMMONIA GAS.

The following method was adopted for the preparation of the gas. Pure ammonium chloride and slaked lime were warmed together. This gave a big yield of gas, which was dried by passing through several U-tubes containing freshly roasted quicklime. It was finally liquified in a container surrounded by a mixture of solid carbon dioxide and absolute alcohol. Thus any permanent gases carried over were not collected, and a pure specimen of liquid ammonia was obtained.

V. DESCRIPTION OF APPARATUS.

The apparatus used for the viscosity experiment is shown in Fig. 2. The gas enters by the tap T_1, and is liquified as previously stated in the bulb A. This was continued until about 6 ccs. of liquid ammonia were condensed. The pressure gauge used was the same as in the first part of the experiment, but now transferred to the entry end of the capillary tube. B is a trap used to prevent the mercury being drawn into the apparatus consequent upon any sudden change of pressure. The small manometer M_1 was used to verify that the exit pressure was atmospheric, which was found to be always the case. The capillary C_1 and tap T_2 served as a means of adjusting the pressure difference. T_3 is a two-way tap connecting to the collecting apparatus R and to the atmosphere. The receiving vessel R was open to the atmosphere through the tube L, which contained glass wool. To prevent temperature changes once steady conditions had been established, the whole apparatus was lagged with cotton wool. For the readings at room temperature the same method for determining the capillary temperature was used as that in calibrating the tube. To obtain the higher temperatures, steam and aniline vapour were used, a distilling apparatus not shown in the figure being set up. It was found that by covering the end corks with tinfoil they resisted the action of the aniline vapour and did not char appreciably. The appropriate liquid (water or aniline) was boiled sufficiently rapidly to produce a free flow of vapour from the exit end, thus ensuring a uniform temperature inside the jacket equal to the boiling point. The jacket was sloped somewhat towards the exit end to allow condensed vapour to drain away. The boiling points of the vapours for the various atmospheric pressures were found from boiling point tables, Kahlbaum's* values being used.

VI. THE VISCOSITY EXPERIMENT.

When enough liquid ammonia was obtained the tap T_1 was closed and the generating apparatus removed. The condensing Dewar *D* was then lowered until sufficient gas had evaporated to sweep all air from the apparatus, the gauge being lowered to clear its tubes and then raised to send a rapid current of ammonia through the capillaries *C* and C_1. The bulb *A* was then surrounded by an empty Dewar flask and the whole heavily wrapped in cotton wool. It was found that, though a suitable driving pressure was soon created, it was not steady enough to allow accurate measurement. This was due to variations in the small quantity of heat reaching the bulb caused by convection currents, etc. This difficulty was overcome by introducing a " dead space " equal to four or five times the volume of gas transmitted during a reading, which acted a sort of " buffer " and gave the required steadiness.

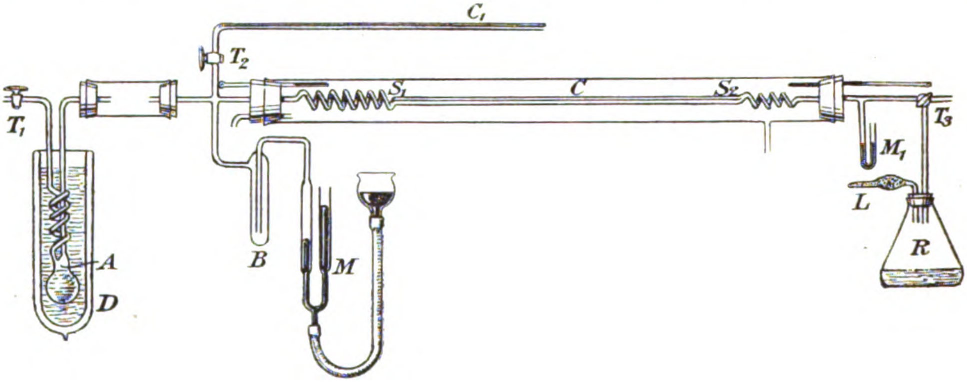


FIG. 2.

Now the critical velocity of transmission for any gas depends on its kinematic viscosity—namely, η/ρ. For ammonia and air this kinematic viscosity is approximately the same. Hence, since the critical velocity for air is given by a pressure difference of 6 cms. of mercury (from first part of the experiment), the pressure difference to be used for ammonia could not exceed this value. The tap T_2 and tube C_1 were used to keep within this range.

Under these conditions the pressure difference remained steady, the greatest variations being usually less than 2·0 per cent. The initial and final portions of the gas were neglected as possibly containing impurities.

The gas, after transpiration, was absorbed in a known volume of standard acid in the receiver *R*. To test whether the gas was completely absorbed, a moistened litmus paper was put over the exit of *L*. This being always unaffected showed that all the ammonia was absorbed. At the end of the " run " the excess acid was titrated with standard Na_2CO_3 solution, methyl orange being used as an indicator. The basis of standardisation of the solutions used was taken to be $N/_{10}HCl$, prepared from a constant boiling mixture of that acid.*

---

* Z. Phs. Chem., 26 (1898).

VII. CALCULATION OF RESULTS.

The transpiration formula in this case gives

$$\eta_t = K_t \frac{(P_1-P_2)(P_1+P_2)}{P_2V_2} = K_t \frac{\delta(2P_2+\delta)}{P_2V_2}$$

where P_2=atmospheric pressure$=P_1-\delta$.

As before, P_2 and δ are converted to cms. of mercury at 0°C. The appropriate value of the constant is obtained from the experimental value, using the relation

$$K_t=K_0(1+3\gamma t)$$

where γ=coefficient of linear expansion of glass=0·000009.

The volume of gas (V_2) at pressure P_2 and the temperature of the jacket is calculated from the weight of gas deduced from the titration results.

Since, however, ammonia does not, especially at atmospheric temperature, behave as a perfect gas, we cannot use the perfect gas equation to determine V_2 from the mass of gas titrated without applying a correction.

Consequently the experimental densities of the gas at various temperatures given by Perman and Davies† were used to obtain this correction.

The values used were—

Temperature.	Litres per gram observed.	Litres per gram PV equation.	Correction.
0°C.	1·2973	1·3161	1·43%
50°C.	1·5473	1·5571	0·64%
100°C.	1·7964	1·7980	0·10%

From this table, by graphing temperatures against correction, the necessary correction at any temperature was found.

The values of the correction thus determined were :—

Temperature.	Correction.
15°C.	1·20 per cent.
100°C.	0·10 per cent.
184°C.	0·0 per cent.

Finally it was necessary to correct the values of the viscosity thus obtained for slipping exactly as in the determination of K.

The correction factors by which the viscosity has to be multiplied are as follows :—

At	15°C.	1·0036
	100°C.	1·0057
	184°C.	1·0073

---

* cf. Halett and Bonner, J. Am. Chem. Soc., 31, pp. 390-393 (1909).

† Proc. Roy. Soc., Vol. 78., p. 34 (1906).

VIII. TABLES OF RESULTS.

Table II gives a specimen series of observations.

TABLE II.

Time.	Temp. of gas.	Barometer.	Manometer A (cms. of Hg)	B.	Volume of gas.	Viscosity.
15 mins.	183·6°C.	75·42 cms.	3·97	5·84	23·20 c.cms.	1 1·7 × 10⁻⁶
10 ,,	183·8°C.	75·74 ,,	1·37	5·65	35·95 ,,	161·7 ,,
9 ,,	183·8°C.	75·72 ,,	1·66	5·85	31·11 ,,	161·1 ,,
9 ,,	183·8°C.	75·70 ,,	1·72	5·93	32·06 ,,	160·5 ,,
10 ,,	183·95°C.	76·06 ,,	3·935	6·07	17·25 ,,	160·8 ,,
10 ,,	183·9°C.	76·03 ,,	4·79	6·21	11·75 ,,	161·3 ,,

TABLE III.

t°C.	$\eta\times10^6$	t C.	$\eta\times10^6$	t°C.	$\eta\times10^6$
15°C.	98·9	100·1°C.	131·0	183·8°C.	161·7
	101·7		130·6		161·7
	101·3		127·7		161·1
	101·8		130·2		160·5
	99·5		127·4		160·8
	100·2		130·2		161·3
	101·5		130·8		
	101·8		128·2		
	97·9				
	100·2				

Mean values :

$\eta_{15}=100{\cdot}5\times10^{-6}$: $\eta_{100\cdot1}=129{\cdot}5\times10^{-6}$: $\eta_{183\cdot8}=161{\cdot}2\times10^{-6}$ C.G.S. units.

The readings at room temperature were corrected to 15°C. by the assumption of a linear rate of change of viscosity with temperature using in conjunction with our own results the mean of Vogel's* and Thomsen's† values at 0°C., viz.: $\eta_0=94{\cdot}3\times10^{-6}$ C.G.S. units (their values were $92{\cdot}6\times10^{-6}$ and $96{\cdot}0\times10^{-6}$ C.G.S. units respectively). For the other two determinations, during which the variations were much smaller, it was sufficient to take the mean temperature for the value.

IX. CALCULATION OF SUTHERLAND'S CONSTANT. DISCUSSION OF RESULTS.

The accepted formula for change of viscosity with temperature is

$$\eta=\frac{KT^{3/2}}{C+T}$$

where C=Sutherland's constant, T=absolute temperature, K=a constant.

Assuming this relation holds, then $KT^{3/2}/\eta=C+T$. Therefore, $T^{3/2}/\eta$ is a linear function of T. The effect of plotting this is shown in Fig. 3. The accuracy of the experiments in relation to the temperature range is not such as to enable Sutherland's law to be tested; but, assuming it to be true, we may make an estimate of the constant by drawing the best straight line through the points on the graph. The value for C thus obtained is 377, but this must be regarded as subject to considerable error, as the points only fit the best straight line with an accuracy of one per cent.

---

* Berlin Dissertation (1914).

† Ann. der Physik., Vol. 36, p. 825.

By extrapolation from the graph, η_0 is found to be equal to $94{\cdot}4 \times 10^{-6}$ C.G.S.

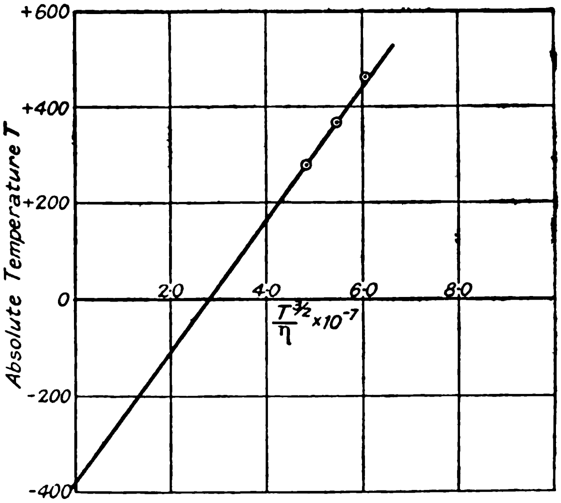


FIG. 3.

units, which compares well with the mean of Vogel's and Thomsen's results quoted above. Prof. Rankine and C. J. Smith* found $\eta_{100} = 130{\cdot}3 \times 10^{-6}$ C.G.S. units, which also agrees well with our value of $129{\cdot}5 \times 10^{-6}$ C.G.S. units; further, assuming $\eta_0 = 94{\cdot}3 \times 10^{-6}$ C.G.S. units, they calculated Sutherland's constant as 370, and, using this result, found the mean collision area ($\bar{A}$) of the ammonia molecule to be $\bar{A} = 0{\cdot}640 \times 10^{-15}$ cms.^{2}. From our data $\bar{A} = 0{\cdot}633 \times 10^{-15}$ cms.^{2}.

DISCUSSION.

Prof. A. O. **RANKINE** said that in published tables of physical constants the values given for different temperatures have often been obtained by different methods and cannot, therefore, be safely used for studying the variation of a given property with temperature. Hence it is important to apply any given method over as wide a range of temperatures as possible. The authors have covered a range of about 170°C., which is very satisfactory.

Mr. F. E. **SMITH** said that the authors' work is a valuable indication that the transpiration method is a simple and reliable one for determining viscosities.

---

* Phil. Mag. 42 (1921)

IV.—VALVE MAINTAINED TUNING FORKS WITHOUT CONDENSERS.

By T. G. HODGKINSON, *A.M.I.E.E.*

Received September 4, 1925.

ABSTRACT.

The valve maintained tuning fork is now a much used piece of apparatus, but the influence of the conductance of the valve electrodes on the design has not been considered. The present paper discusses the design of valve maintained tuning forks without condensers and shows that the conductance of the valve grid decides the direction in which the electrode coils must be wound; and also that it is advantageous, particularly in the case of low frequency forks, to interpose transformers between the valve electrodes and the fork magnets.

THE valve controlled tuning fork was originated by Eccles, and demonstrated before the Physical Society.*

The method was investigated by Butterworth,† who dealt with "untuned" and "tuned" systems, and evaluated the very small differences between the note frequency of the maintained system and the *true fork note.*

The work following employs Butterworth's methods and notation to some extent to amplify the case of the "untuned" fork system, and to clear away ambiguity with regard to the direction of winding of the electrode coils; also to deal with a system employing transformers between the valve electrodes and the fork magnet coils.

The transformer system has obvious advantages for low-frequency forks in that, apart from the additional winding space and improved space factor it provides, it is possible to adjust the phase of the driving current in a way to reduce the difference between the note of the maintained system and the *true fork note* to zero, and in this respect is similar to condenser tuned systems.

Notation.

Mass of fork supposed collected at end of prong	α	
Frictional force per unit velocity	β	
Control force per unit displacement	γ	
Force in magnet gap per unit current in anode coil	A_1	
Force in magnet gap per unit current in grid coil	A_2	
Plate coil resistance and inductance	r_1	L_1
Grid coil resistance and inductance	r_2	L_2
Plate and grid conductances	s_1	s_2
Plate and grid currents	i_1	i_2

The fork is controlled by the electrode coils, which are wound on pole pieces of a magnet system and arranged close to the prongs of the fork, as shown in Fig. 1.

The effect of the iron losses adds a determinate amount to the effective resistance of the coils, and this amount is supposed included in the resistances r_1 and r_2. The effective inductances of the coils are also reduced by a determinate amount by the iron losses, and the symbols L_1 and L_2 are intended to indicate the reduced values.

---

* Proc. Phys. Soc., Vol. 31, p. 260 (1919).

† Proc. Phys. Soc., Vol. 32, p. 345 (1920).

D is the time operator $\delta/\delta t$, and the equation of motion of the fork system is

$$(\alpha D^2+\beta D+\gamma)y=A_1i_1+A_2i_2,$$

where y is the displacement of the mass α.

The currents are supposed counter clockwise, and the coils are similarly wound—i.e., connected in such a way that a current passing from the grid to the plate would maintain flux in the same direction in the magnet system.

The back E.M.F. in the anode coil due to movement of the fork prong is

$$A_1Dy=\frac{A_1^2Di_1+A_1A_2Di_2}{\alpha D^2+\beta D+\gamma}$$

and, similarly, the back E.M.F. in the grid coil is

$$A_2Dy=\frac{A_1A_2Di_1+A_2^2Di_2}{\alpha D^2+\beta D+\gamma}$$

This notation is Butterworth's, and the equation resulting from a systematic solution of the circuit, which is given below, differs from his in the sign of the valve magnification factor term, and in that it includes a discussion of the effect of the valve conductances.

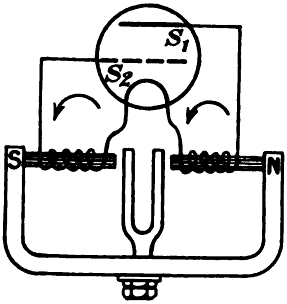


FIG. 1.—FORK SYSTEM WITH MAGNET COILS DIRECTLY CONNECTED TO VALVE ELECTRODES.

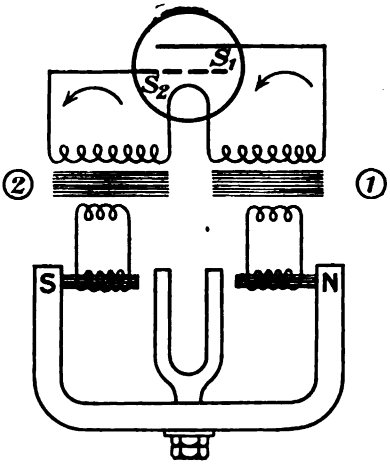


FIG. 2.—FORK SYSTEM WITH TRANSFORMERS BETWEEN THE VALVE ELECTRODES AND FORK MAGNET COILS.

The circuit equation is

$$\Big[(1/s_1+r_1+L_1D)(1/s_2+r_2+L_2D)(\alpha D^2+\beta D+\gamma)+$$
$$(1/s_1+r_1+L_1D)A_2^2D+(1/s_2+r_2+L_2D)A_1^2D-\frac{m}{s_2}A_1A_2D\Big]i_1i_2=0 \quad (1)$$

m is the valve magnification factor, or $\delta i_1/\delta V_g \div \delta i_1/\delta V_p$, where V_g and V_p are grid and plate volts respectively.

We are only concerned with discussing this equation with regard to our own particular problem, remembering that the decay factor of the fork should be a very small quantity. The force in a magnet gap per unit current A is something like a linear function of the number of turns on the coil, and A_1^2 is conveniently written X_1L_1. In the same way, $A_2^2=X_2L_2$, and if we write $W_F^2=\gamma/a$, $-W^2=D^2$,

$$\frac{L_1s_1W_F}{1+r_1s_1}=b_1 \text{ and } \frac{L_2s_2W_F}{1+r_2s_2}=b_2$$

we can separate the equation (1) into frequency and condition equations in the popular manner to make

Frequency Equation.

$$\left(1-b_1b_2\frac{W^2}{W_F^2}\right)\left(1-\frac{W^2}{W_F^2}\right)-\frac{\beta}{aW_F}\left(b_1+b_2+\frac{b_1b_2}{\beta W_F}\overline{X_1+X_2}\right)\frac{W^2}{W_F^2}=0 \quad . \quad . \quad . \quad . \quad (2)$$

Condition Equation.

$$(b_1+b_2)\left(1-\frac{W^2}{W_F^2}\right)+\frac{\beta}{aW_F}\left(1-b_1b_2\frac{W^2}{W_F^2}+\frac{X_1b_1+X_2b_2}{\beta W_F}-\frac{m}{1+r_2s_2}\cdot\frac{A_2\,b_1X_1}{A_1\,\beta W_F}\right)\lessgtr 0 \quad (3)$$

The two signs of the condition equation $\lessgtr 0$ depend on the solution of the frequency equation selected for substitution therein—i.e., if the solution of the frequency equation is below the true fork note, the upper sign is required, and vice versa.

Ignoring small quantities, the useful solution of the frequency equation is

$$1-\frac{W^2}{W^2_F}=\frac{\beta/aW_F}{1-b_1b_2}\left(b_1+b_2+\frac{b_1b_2}{\beta W_F}\overline{X_1+X_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

β/aW_F need only be a small quantity like 0·001; b_1 will be made approximately unity in order to use the valve effectively, and b_2 can be made small by working on a negative grid. The values of $X_1/\beta W_F$ and $X_2/\beta W_F$ will transpire subsequently, but will be something like, or less than, unity.

Substituting from equation (4), the *Condition Equation* is

$$(1+b_1^2)(1+b_2^2)-\frac{1}{\beta W_F}\left\{\frac{m}{1+r_2s_2}\;\frac{A_2}{A_1}(1-b_1b_2)X_1b_1-(1+b_2^2)X_1b_1-(1+b_1^2)X_2b_2\right\}$$
$$\lessgtr 0 \quad . \quad . \quad (5)$$

If the product b_1b_2 is appreciably less than unity, the frequency solution gives a note slightly lower (the difference is very small) than the true fork note, and if $X_2=X_1$

$$\frac{X_1}{\beta W_F}>\frac{(1+b_1^2)(1+b_2^2)}{\dfrac{m}{1+r_2s_2}\;(1-b_1b_2)b_1-(1+b_2^2)b_1-(1+b_1^2)b_2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The coils require to be similarly wound—i.e., $A_2=A_1$—and this case includes the non-conducting grid system as a special case.

If the grid conductance is negligible

$$1-W^2/W_F^2=\frac{\beta}{aW_F}\,b_1 \text{ and } \frac{X_1}{\beta W_F}>\frac{1+b_1^2}{b_1\overline{m-1}}$$

$\delta/\delta b_1 \dfrac{X_1}{\beta W_F}$ is negative until $b_1=1$, so that the minimum value of $\dfrac{X_1}{\beta W_F}>\dfrac{2}{m-1}$

Guess m is 7 and $\dfrac{X}{\beta W_F}>1/3$.

This is the ideal valve system, of course, and a value for the grid conductance increases $X/\beta W_F$ appreciably.

In a special case, say $b_1=b_2$,

$$\frac{X_1}{\beta W_F}>\frac{(1+b_1^2)^2}{b_1\left[\frac{m}{1+r_2s_2}(1-b_1^2)-2(1+b_1^2)\right]} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

Guess $\dfrac{m}{1+r_2s_2}=6$, and the best value for b_1 works out about 1/3, and $X_1/\beta W_F>1{\cdot}19$.

Working on positive grids and with large inductances so that the product b_1b_2 is appreciably greater than unity, the note of the maintained system is slightly higher than the true fork note.

$$1-W^2/W_F^2=-\frac{\beta/aW_F}{b_1b_2-1}\left(b_1+b_2+\frac{b_1b_2}{\beta W_F}\overline{X_1+X_2}\right) \quad . \; . \; . \; . \; . \quad (8)$$

The coils now require to be oppositely wound, and if $X_2=X_1$ and $A_2=-A_1$

$$\frac{X_1}{\beta W_F}>\frac{(1+b_1^2)(1+b_2^2)}{\frac{m}{1-r_2s_2}(b_1b_2-1)b_1-(1+b_2^2)b_1-(1+b_1^2)b_2} \quad . \; . \; . \; . \; . \; . \quad (9)$$

Guess $\dfrac{m}{1+r_2s_2}=5$ and $b_1=b_2$, the best value of b_1 works out about 3·125 and

$\dfrac{X_1}{\beta W_F}>1{\cdot}66$.

The guesses at $\dfrac{m}{1+r_2s_2}$ probably favour the latter case to some extent, but the general results are borne out by experiment; indeed, fork systems can be designed so that when the valve filament is relatively dull and the grid is negative the fork is maintained with the coils *similarly* wound, while, if the valve filament is bright and the grid is positive, the fork is only maintained when the grid coils are *oppositely* wound.

The special case when the product b_1b_2=unity is not a profitable one. The frequency solution is $1-W^2/W_F^2=\pm\sqrt{\dfrac{\beta}{aW_F}}$, and the system is correspondingly difficult to support in vibration.

The decay factor of a higher frequency fork is difficult to measure directly, but can be determined by the method advocated by A. Campbell,* using a vibration galvanometer connected to a coil, the induction of which is varied by the movement of the fork.

This method was investigated analytically by R. Ll. Jones.†

Alternatively, the quantity A^2/β can be measured as a part of the effective resistance of the magnet coil tested on a bridge at the resonant frequency of the fork; but this measurement requires great care and careful measurement, on the same bridge, of the effective copper and iron resistances with the fork held still. With lower frequency forks the decay factor can be determined with a microscope and stop watch.

If the iron losses for a magnet coil may be represented as due to a circuit completely linked with the coil and having resistance r_1 and inductance l_1, then the part of the effective resistance of the coil due to iron losses is $\frac{LWI}{1+I^2}$ and the effective inductance is $\frac{L}{1+I^2}$, where L is the inductance of the magnet coil and I is $\frac{l_1 W}{r_1}$

I can be predetermined for a specific case in terms of the hysteresis coefficient, permeability, flux densities and Joulean resistance, and may be as much as 0·2, but should be less.

The importance of keeping the losses small is apparent by their effect in reducing $b=\frac{LsW}{1+rs}$ and $\frac{m}{1+r_2s_2}$

$A^2/L=X$ will have something of the form

$$X=\frac{B_0^2}{4\pi R_g}\cdot\frac{R_a}{R_a+R_g}$$

where B_0 is the flux density in the gap, R_a is the leakage reluctance, R_g is the gap and iron circuit reluctance.

The importance of keeping the leakage reluctance large is obvious.

The 1,000 ~ fork made by the Cambridge Scientific Instrument Co. has the requirements of design for an "untuned" system working on a negative grid, and although this fork is provided with condensers it is maintained in oscillation without them.

Transformer Coupled System.

The dimensions of the higher frequency "commercial" forks lend themselves to the design of valve control systems, but low frequency forks are more difficult.

The principal difficulty is that of making the impedance of the anode magnet coil compete with the anode resistance without making the copper and iron losses impossibly large and the leakage reluctance too small. Again, the decay factors of these forks are frequently greater than those of higher frequency forks.

The impedance difficulty can be overcome by interposing suitable transformers between the valve electrodes and the magnet coils. In addition to the advantages enumerated earlier of additional and improved space factors and capability of adjusting the difference between the note of the system and the true fork note, the steady flux may be provided by direct current in the magnet coils, and so conveniently adjusted for experimental purposes.

---

* Proc. Phys. Soc., Vol. 31, p. 87 (1919).

† Proc. Phys. Soc., Vol. 34, p. 67 (1922).

Notation.

Resistance and inductance of valve winding of transformer (1) ...	r_1 l_1
Resistance and inductance of valve winding of transformer (2) ...	r_2 l_2
Resistance and inductance of fork winding of transformer (1) ...	ρ_1 λ_1
Resistance and inductance of fork winding of transformer (2) ...	ρ_2 λ_2
Mutual coupling transformer (1)	M_1
Mutual coupling transformer (2)	M_2
Resistance and inductance of fork magnet coil (1)	P_1 L_1
Resistance and inductance of fork magnet coil (2)	P_2 L_2

In what follows the transformers have been dealt with as without leakage, although this does not affect the conclusion drawn if the leakage is small and is regarded as included in the fork magnet coil inductances.

A systematic solution of the circuits gives the differential equation

$$\Big[\{(1+s_1\overline{r_1+l_1D})(P_1+\rho_1+\overline{L_1+\lambda_1D})-s_1M_1^2D^2\}\{(1+s_2\overline{r_2+l_2D})(P_2+\rho_2+\overline{L_2+\lambda_2D})-s_2M_2^2D^2\}$$

$$+\{(1+s_1r_1+l_1D)(P_1+\rho_1+L_1+\lambda_1D)-s_1M_1^2D^2\}(1+s_2r_2+l_2D)\frac{A_2^2D}{aD^2+\beta D+\gamma}$$

$$+\{(1+s_2\overline{r_2+l_1D})(P_2+\rho_2+\overline{L_2+\lambda_2D})-s_2M_2^2D^2\}(1+s_1\overline{r_1+l_1D})\frac{A_1^2D}{aD^2+\beta D+\gamma}$$

$$-s_1M_1M_2D^2\frac{mA_1A_2D}{aD^2+\beta D+\gamma}\Big]i_1i_2=0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (10)$$

Those who have read Butterworth's Paper referred to, or who have analysed fork circuits, will recognise this equation as similar in form to that of a fork circuit with condensers across the electrodes; and, indeed, the transformer coupled system behaves like a condenser tuned system, in that it is capable of reducing the difference between the note maintained by the system and the true fork note.

Adding to the notation

$$\frac{P_1+\rho_1}{L_1W_F}=a_1 \qquad \frac{L_1+\lambda_1}{L_1}=c_1 \qquad \frac{l_1s_1W_F}{1+r_1s_1}=b_1$$

$$\frac{P_2+\rho_2}{L_2W_F}=a_2 \qquad \frac{L_2+\lambda_2}{L_2}=c_2 \qquad \frac{l_2s_2W_F}{1+r_2s_2}=b_2$$

and separating the phases.

The *Frequency Equation* becomes

$$\left(1-\frac{W^2}{W_F^2}\right)\left[\left(a_1-b_1\frac{W^2}{W_F^2}\right)\left(a_2-b_1\frac{W^2}{W_F^2}\right)-(c_1+a_1b_1)(c_2+a_2b_2)\frac{W^2}{W_F^2}\right]$$

$$-\frac{\beta}{aW_F^2}\frac{W^2}{W_F^2}\left[\begin{array}{l}\left(a_1-b_1\frac{W^2}{W_F^2}\right)(c_2+a_2b_2)+\frac{X_2}{\beta W_F}\left(c_1+a_1b_1+b_2a_1-b_1\frac{W^2}{W_F^2}\right)+\\ \left(a_2-b_2\frac{W^2}{W_F^2}\right)(c_1+a_1b_1)+\frac{X_1}{\beta W_F}\left(c_2+a_2b_2+b_1a_2-b_2\frac{W^2}{W_F^2}\right)\end{array}\right]=0 \qquad (11)$$

and *Condition Equation*

$$\left(1-\frac{W^2}{W_F{}^2}\right)\left[\left(a_1-b_1\frac{W^2}{W_F{}^2}\right)(c_2+a_2b_2)+\left(a_2-b_2\frac{W^2}{W_F{}^2}\right)(c_1+a_1b_1)\right]+$$

$$\beta/aW_F\left[\begin{array}{l}\left(a_1-b_1\frac{W^2}{W_F{}^2}\right)(a_2-b_2W^2/W_F{}^2)-(c_1+a_1b_1)(c_2+a_2b_2)\frac{W^2}{W_F{}^2}+\\ \frac{X^2}{\beta W_F}\left\{a_1-b_1\frac{W^2}{W_F{}^2}-b_2\frac{W^2}{W_F{}^2}(c_1+a_1b_1)\right\}+\\ \frac{X_1}{\beta W_F}\left\{a_1-b_1\frac{W^2}{W_F{}^2}-b_1\frac{W^2}{W_F{}^2}(c_2+a_2b_2)+\frac{mb_1}{1+r_2s_2}(c_1-1)\frac{W^2}{W_F{}^2}\cdot\frac{M_2A_2L_1}{M_1A_1L_2}\right\}\end{array}\right]=0 \quad (12)$$

There are too many quantities in these equations to be discussed independently, but if we make the transformers of the two electrodes similar and the magnet coils similar, $a_1=a_2$ and $c_1=c_2$, but b_1 and b_2 are dependent on the valve electrodes.

Write $\frac{b_1-a_1}{c_1+a_1b_1}=\varphi_1$ and $\frac{b_2-a_2}{c_2+a_2b_2}=\varphi_2$, $X_2=X_1$, and the *Frequency Equation* becomes

$$1-\frac{W^2}{W_F{}^2}=\frac{\beta/aW_F}{1-\varphi_1\varphi_2}\left[\varphi_1+\varphi_2-\frac{2X}{\beta W_F}\cdot\frac{(1-a\overline{\varphi_1+\varphi_2}-c\varphi_1\varphi_2)}{c+a^2}\right] \quad . \quad . \quad . \quad . \quad (13)$$

and substituting this value in the condition equation the condition equation becomes

$$\frac{X}{\beta W_F}>\frac{(1+\varphi_1{}^2)(1+\varphi_2{}^2)}{\frac{c-1}{c+a^2}\left[\pm\frac{m}{1+r_2s_2}\frac{(c\varphi_1+a)(1-a\varphi_2)(1-\varphi_1\varphi_2)}{c+a^2}-\varphi_1(1+\varphi_2{}^2)-\varphi_2(1+\varphi_1{}^2)\right]}$$

$$-\frac{2a}{c+a_2}(1+\varphi_1{}^2)(1+\varphi_2{}^2) \quad . \quad . \quad (14)$$

When the product $\varphi_1\varphi_2$ is small compared with unity, m requires the positive sign—i.e., the circuits are similarly wound; but when $\varphi_1\varphi_2$ is greater than unity, m requires the negative sign, or the circuits are oppositely wound.

If a is negligibly small, the frequency equation becomes

$$1-\frac{W^2}{W_F{}^2}=\frac{\beta/aW_F}{1-\varphi_1\varphi_2}\left(\varphi_1+\varphi_2+\frac{2X}{\beta W_F}(\varphi_1\varphi_2-1/c)\right). \quad . \quad . \quad . \quad . \quad (15)$$

and the *Condition Equation*

$$\frac{X}{\beta W_F}>\frac{(1+\varphi_1{}^2)(1+\varphi_2{}^2)}{\frac{c-1}{c}\left[\pm\frac{m\varphi_1}{1+r_2s_2}(1-\varphi_1\varphi_2)-\varphi_1(1+\varphi_2{}^2)-\varphi_2(1+\varphi_1{}^2)\right]} \quad . \quad . \quad . \quad . \quad (16)$$

and whatever has been said of the optimum values of b_1 in the case of the direct coupled system applies to φ in the case of this transformer coupled system.

The optimum value of c in this transformer case is limited only by practical considerations, but a value for a reduces the optimum values of both φ and c very appreciably.

Returning to the general case of equations (13) and (14), notice that if the product $\varphi_1\varphi_2$ is less than unity it is possible to adjust φ and c to make the difference $1-\frac{W^2}{W_F{}^2}=0$.

Indeed, if a_1 has value this condition may easily give the lowest value of $X/\beta W_F$ in the condition equation.

The equation connecting φ and c to achieve this result is

$$\frac{m}{1+r_2s_2}\cdot\frac{c-1}{c+a^2}(1-a\varphi_2)(a+c\varphi_1)(\varphi_1+\varphi_2)$$
$$-(1+\varphi_1^2)(1+c\varphi_2^2)-(1+\varphi_2^2)(1+c\varphi_1^2)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

a is a function of c for any particular frequency and any particular space factor so that this equation becomes a quadratic in c.

If the grid conductance is entirely negligible, $b_2=0$ and $\varphi_2=-a/c$, and the *Frequency Equation* (13) reduces to

$$1-\frac{W^2}{W_F^2}=\frac{\beta/aW_F}{1+a\varphi_1/c}\left(\varphi_1-a/c-2/c\,\frac{X}{\beta W_F}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

While the *Condition Equation* (14) becomes

$$\frac{X}{\beta W_F}>\frac{1}{\frac{c-1}{c+a^2}\,\overline{m-1}\left(\frac{a/c}{1+a^2/c^2}+\frac{\varphi_1}{1+\varphi_1^2}\right)-\frac{2a}{c^2+a^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If $a=fc$ the special condition equation (17) becomes

$$c=\frac{2+\overline{m+1}\,\varphi_1^2-\overline{m-1}f^2}{(m-1-2f^2)\,\varphi_1^2-\overline{m+1}f^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The value of φ_1 which gives the smallest value for $X/\beta W_F$ does not give the true fork note. As an example, if $f=0{\cdot}2$ and $m=7$, say $c=4$.

The optimum value of φ_1 is unity.

$$1-W^2/W_F^2=0{\cdot}59\beta/aW_F \text{ and } \frac{X}{\beta W_F}>0{\cdot}39.$$

On the other hand, if $\varphi_1=0{\cdot}44$

$$1-W^2/W_F^2=0 \text{ and } \frac{X}{\beta W_F}>0{\cdot}48.$$

The negative grid gives, of course, the ideal transformer case, and a value for b_2 increases $\frac{X}{\beta W_F}$ very appreciably.

If the grid conductance is equal to the plate conductance $\varphi_2=\varphi_1$, and the Frequency Equation (13) becomes

$$1-\frac{W^2}{W_F^2}=\frac{2\beta/aW_F}{1-\varphi^2}\left(\varphi-\frac{X}{\beta W_F}\cdot\frac{(1-2a\varphi-c\varphi^2)}{c+a^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and the Condition Equation (14) becomes

$$\frac{X}{\beta W_F}>\frac{1}{\frac{c-1}{c+a^2}\left\{\frac{m}{1+r_2s_2}\cdot\frac{(1-a\varphi)(1-\varphi^2)(a+c\varphi)}{(1+\varphi^2)^2(c+a^2)}-\frac{2\varphi}{1+\varphi^2}\right\}-\frac{2a}{c+a^2}} \quad . \quad . \quad . \quad . \quad (22)$$

As an example, say $\frac{m}{1+r_2s_2}=6$ and $f=0\cdot2$. The optimum value of c is in the neighbourhood of 4·4, and the optimum value of $\varphi=0\cdot13$.

$$1-\frac{W^2}{W_F^2}=0\cdot59\beta/aW_F \quad \text{and} \quad \frac{X}{\beta W_F}\succ2\cdot35.$$

The value of φ giving the true fork note is 0·235, and under these conditions $\frac{X}{\beta W_F}\succ2\cdot87$.

When the product $\varphi_1\varphi_2\succ1$, m requires the negative sign (i.e., the circuits require to be oppositely wound), the values of $X/\beta W_F$ increase very rapidly, and there is no opportunity of equating the note of the system to the true fork note.

As an example, say $f=0\cdot1$ and $\varphi_1=\varphi_2=2$; the optimum value of c is in the neighbourhood of 1·4, and the system would not work on the valve we have used for the other systems, with $m=7$. If, however, $\frac{m}{1+r_2s_2}=12$, or double the magnification factor of the valve used previously

$$1-\frac{W^2}{W_F^2}=-12\beta/aW_F \quad \text{and} \quad \frac{X}{\beta W_F}\succ5\cdot46.$$

If β/aW_F is large, this would not be a case we could deal with in this approximate way; but the case is not a profitable one in any sense.

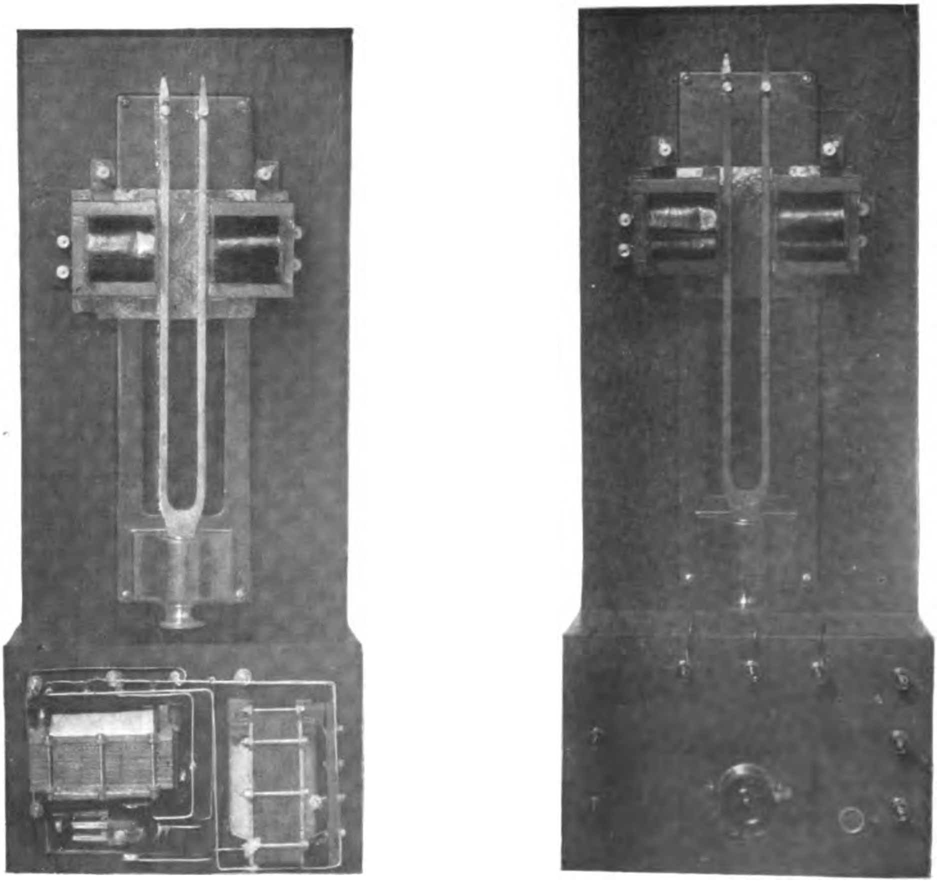
In the foregoing work an effort has been made to determine the best system of design for low frequency forks. It requires no analysis to discover that losses should be kept small or that systems working on negative grids are better than those working on conducting grids; however, it is useful to know to what extent these losses may be incurred. If the grid is sufficiently negative to prevent appreciable rectification, the grid conductance need not concern the design at all. On the other hand, a special grid battery is an unnecessary expense, and a rectifying grid is easily dealt with in design. Indeed, it is not until positive volts are put on grids that grid conductances require special consideration, unless coil resistances are too large and the product r_2s_2 has a significant value.

A design for a *direct coupled* system working on a reception valve with grid conductance (say about one-fifth the plate conductance) would make $\frac{m}{1+r_2s_2}=6$ and $\frac{l_1s_1W_F}{1+r_1s_1}=0\cdot7$.

This would give with similar magnets $\frac{X}{\beta W_F}=0\cdot51$ and $1-W^2/W_F^2=1\cdot05\ \beta/aW_F$.

With low frequency forks $\frac{l_1s_1W_F}{1+r_1s_1}=0\cdot7$ may be a difficult achievement for a *direct coupled* system, but easy with a closed iron circuit transformer between electrodes and magnets.

The improved space factor of the magnet coils using heavier wire together with the added space of the transformer makes small values of $a=fc=\frac{P+\rho}{LW_F}$ possible.



PHOTOGRAPH OF FORK SHOWING TRANSFORMERS.

[To face page 33

If a battery is used to provide the steady flux, the magnet wire can be selected for small voltages.

A design for a transformer coupled system is embodied in the quantities

$$c=4 \qquad \text{or} \qquad \lambda/L=3$$

$$a=1 \qquad \text{or} \qquad f=0{\cdot}25$$

$$\frac{m}{1+r_2s_2}=6, \quad \varphi_1=0{\cdot}35, \quad \varphi_2=-0{\cdot}05.$$

This, with similar magnets on both electrodes, would make

$$\frac{X}{\beta W_F}=0{\cdot}97 \quad \text{and} \quad 1-W^2/W_F^2 \text{ negligible.}$$

An actual example of a 50 cycle fork design is given below.

Similar Transformers.

Electrode winding	14,000 turns	40 S.W.G.	copper.
Magnet circuit	500 ,,	22 ,,	,,
Magnet coils	1,000 ,,	22 ,,	,,

$l=144$ henries $r=4{,}300$ ohms including iron losses
$\lambda=0{\cdot}23$,, $\rho=4{\cdot}4$,, ,, ,,
$L=0{\cdot}17$,, $P=6{\cdot}2$,, ,, ,,

This makes $c=2{\cdot}35$, $a=0{\cdot}2$, $\varphi_1=0{\cdot}55$

The steady flux is provided by a 2 volt battery, and the fork works well on negative or rectifying grids, with any plate voltage above 20 volts.

The fork prongs are 31·5 cm. long, 0·6 cm. deep by 1·5 cm. wide, the magnet coils are wound on E-shaped stalloy stampings with an effective area of 2 square cms.

β/aW_F measured with a microscope and stop watch is 0·002, and the valve is an R7, with a magnification factor about 7·5 and a plate conductance $4{\cdot}4\times10^{-5}$ mhos.

This design is generous in material, but the value of c is roughly right to give the true fork note with a non-conducting grid.

NOTE ADDED NOVEMBER 21, 1925.

The true fork note frequency is $50(1+0{\cdot}00007)$. The maintained note, with the valve grid connected to the negative end of the filament battery and for an amplitude of vibration of 0·7 mm. at the ends of the prongs, is $50\,(1-0{\cdot}00012)$. For an amplitude of 2 mm. it is $50\,(1-0{\cdot}00056)$. These are comparative measurements only, and have an accuracy ±0·002 per cent. approx. The difference between the true fork note and the 0·7 mm. amplitude maintained note gives a value for $1-W^2/W_F^2=0{\cdot}00038$ or $0{\cdot}19\ \beta/aW_F$, a value that would have been impracticable with a direct-coupled system.

I should like to express my indebtedness to Mr. A. Hinchliffe, whose help in the work has been invaluable, and to the Director of Artillery for his permission to offer the Paper for publication.

DISCUSSION.

Dr. W. H. ECCLES said that every one who wishes to use valve maintained forks with precision must read Mr. Butterworth's Paper on the subject, but that Paper does not explain the ambiguity which exists as to the direction of winding of the grid coil. This puzzle has been cleared up by the author, who has also shown how account must be taken of the valve characteristics in designing the apparatus, and how to secure that the maintained frequency shall be the true frequency of the fork. The latter point is particularly important when the harmonics of the fork frequency are employed: thus it is possible to utilise the twenty-ninth harmonic of a 1,000∾ fork, giving a frequency of 60,000∾. In this way standards can be obtained and oscillations generated over a wide range of the wireless spectrum, at constant and accurately known frequencies.

Dr. C. V. DRYSDALE said that he had long been interested in stroboscopic methods of measurement, but these have always suffered from the defect that the rate of a fork is varied by the means adopted for maintaining vibration. Dr. Eccles' invention of the valve-maintained fork is of great importance as a solution of this difficulty, and the author is to be congratulated on having put the matter on a satisfactory quantitative basis.

Mr. S. BUTTERWORTH (communicated): I have read Mr. Hodgkinson's Paper with great interest. He is quite right when he states that in my Paper on the same subject I gave an erroneous sign to the proper direction of winding for the grid and anode coils in order to maintain the fork in vibration. It may be of interest to point out that the quantities b_1 and b_2 represent the ratio of reactance to resistance in the plate and grid circuits respectively, so that the condition given in the simplest case dealt with by Mr. Hodgkinson (the case of no grid current and no transformers) is that for the greatest ease of maintenance the reactance of the anode circuit should be equal to its resistance. Also, if we remember that the motional impedance of a fork system may be represented by an inductance, capacity and conductance in parallel, the condition that the system will produce sustained vibrations (when the reactance-resistance condition above is satisfied) is that the mutual conductance of the valve shall exceed the anode conductance by an amount at least twice the motional conductance representing the losses in the fork system. The treatment of the case where transformers are used has been very thorough. If we idealise this case, and suppose the transformers perfectly coupled, free from loss, and with fork windings of impedance large compared with the coils driving the fork, then the use of the electrical equivalent of the motional impedance of the fork enables us to show that the transformer system may be replaced by a system free from transformers, in which all the impedances are multiplied by the square of the ratio of transformation. This for equal anode and grid transformers. This is a result something like that arrived at by Mr. Hodgkinson in equation (16). I do not quite understand the particular virtue of making the actual fork frequency exactly equal to the free fork frequency. The special value of these systems lies in their constancy, and, as has been pointed out by Mr. Dye, certain adjustments of the valve voltages may be made to enhance the steadiness. These adjustments are the more readily carried out if the valve system is working well above the limits of maintenance. The reason for supplying condensers to fork systems at 1,000 frequency is partly to enable a greater load to be taken from the system and partly to have greater ease in carrying out the adjustments for the steadiest condition.

AUTHOR'S reply (communicated): Replying to Prof. Eccles, I have not discussed the use of harmonics, being mainly concerned with producing a low-frequency source in imitation of the noise made by an aeroplane.

The fact that the fork is barely audible even when the fundamental amplitude is very large is evidence of the approximate purity of the note.

The actual difference between the maintained note and the true fork note is not so important as is the constancy of the maintained note and its dependence on such factors as filament emission, gap field, etc. I have included consideration of the valve conductances in the investigation of condenser tuned systems for my own information, and, in general, well-designed condenser tuned systems give smaller differences between the maintained note and the fork note than systems without condensers; however, there is nothing to prevent the tuning of the transformer coupled system, possibly with benefit to the constancy of the note.

I thank Dr. Drysdale for his appreciation of the aim of the Paper, which was to emphasise the importance of the electrode conductances without encroaching too much on ground so thoroughly prospected by Prof. Eccles and Mr. Butterworth.

I wish to thank Mr. Butterworth also for his very interesting communication, and, in reply to his implied question, I think it is an advantage to know that the transformer system is capable of design so that there is only a small difference between the maintained note and the fork note. Although this capability does not necessarily improve the constancy of the note, it does not diminish it, and allows a certain measure of adjustment.

I thoroughly appreciate the effect of condensers in improving the maintenance conditions of tuning forks, and my reference to the Cambridge Co.'s fork was by way of illustration only.

V.—THE TIMES OF "SUDDEN COMMENCEMENTS" (S.C.s) OF MAGNETIC STORMS: OBSERVATION AND THEORY.

By C. CHREE, *Sc.D., LL.D., F.R.S.*

Received October 8, 1925.

ABSTRACT.

An earlier Paper (Proc. Phys. Soc., Vol. 26, 1914, p. 137) discussed a number of data for the times of occurrence of the "Sudden Commencements" (S.C.s) of magnetic storms which had been published by Dr. L. A. Bauer in "Terrestrial Magnetism," and came to a conclusion adverse to Dr. Bauer's claim that S.C.s were propagated from east to west or west to east, with velocities of from 100 to 200 kilometres per second. Since that date Papers on the subject have been published by Prof. S. Chapman and Fr. Rodés, of the Ebro Observatory, propounding theories differing from one another and from Dr. Bauer's. In a recent Paper Dr. Bauer and Mr. W. J. Peters have re-discussed the subject. They conclude that the motion in longitude is much more rapid than according to Dr. Bauer's original estimate, and suggest that is is really a case of propagation from the magnetic equator towards either magnetic pole.

The Section of Terrestrial Magnetism and Electricity of the International Union of Geodesy and Geophysics has recently approved a scheme aiming at the construction and use of special instruments to find out whether S.C.s have a finite rate of propagation. The present Paper discusses the whole subject, partly with a view to facilitating a decision as to the new apparatus and the stations most suitable for the investigation.

§ 1.

THE question whether "sudden commencements" (S.C.s)—the rapid movements which often appear as precursors of magnetic storms—occur simultaneously over the earth, or are propagated with a velocity small compared with that of light, is of much interest to magneticians. It is obviously of fundamental importance in any theory of magnetic storms. The fact that the times of occurrence of an S.C. at different parts of the earth agree to within a few minutes has long been accepted. That the times differ to an extent measurable by ordinary magnetographs seems to have been first suggested by Dr. L. A. Bauer.* From a consideration of a variety of S.C.s recorded prior to 1910, he concluded that magnetic storms do not begin at precisely the same instant all over the earth. To quote his own words, (l.c., p. 232): "The abruptly beginning ones (i.e., S.C.s) . . . appear to progress . . . more often eastwardly, though also at times westwardly, at a speed of about 100 km. to 200 km. per second, so that if a complete circuit of the earth were made it would require, on the average, between seven and three minutes." Mr. R. L. Faris,† of the U.S. Coast and Geodetic Survey, from an investigation of 15 S.C.s, as recorded between 1906 and 1909 at the Survey's five observatories, supported Dr. Bauer's conclusion, obtaining 3½ minutes as the mean time of propagation round the earth. After examining Mr. Faris' data critically, the present writer‡ ventured on the opinion that the differences in the times recorded were most likely due to instrumental or observational causes. Shortly afterwards Dr. Bauer issued an invitation to magnetic observatories to send him the times for the fifteen S.C.s selected by Mr. Faris, as derived at each observatory from the curves of that observatory. A number of observatories responded, and Dr. Bauer published the data sent him in the June and September issues of "Terrestrial Magnetism" for 1911. The September issue also contained a revised set of data for the Coast and Geodetic Survey's observatories. In explanation of these Dr. Bauer quoted a request he had addressed to the Superintendent of the Survey to "furnish time scalings of all the disturbances . . . taking into consideration the specimen curves from Potsdam and Kew, the tracings of which are enclosed herewith." "I would suggest," he added, "that chief consideration be paid to the Potsdam curves, the precise point of scaling of which has been indicated by the observer (Dr. Venske)."

---

* "Terrestrial Magnetism," Vol. 15, pp. 9, 111, etc. (1910).

† "Terrestrial Magnetism," Vol. 15, p. 93.

‡ Proc. Phys. Soc., Vol. 23, p. 49.

§ 2.

The data thus published by Dr. Bauer have been discussed, following the historical order, by Prof. G. Angenheister,* myself,† Prof. S. Chapman,‡ and Fr. Rodes§ of Tortosa, and now finally by Dr. Bauer and Mr. W. J. Peters.|| The two earlier discussions were concerned mainly with the bearing of the data on Dr. Bauer's theory, but I also considered the possibility of propagation north and south. The conclusions reached by Prof. Angenheister and myself were unfavourable to Dr. Bauer's theory. Prof. Chapman also drew conclusions (l.c., p. 210) unfavourable to this theory, but he was mainly concerned in presenting an alternative theory. Supposing magnetic storms to be due to discharges of ions from the sun, he considered what would happen if a stream of ions rotated with the sun in the manner suggested by the 27-day interval in magnetic storms. On this view the S.C. might represent the engulfing of the earth in the ionic stream. As the earth's period round the sun is 365 days, and that of the stream only 27, the stream overtakes the earth, and its advance edge will cross the earth from one end of a diameter to the other in about 30 seconds. On this view there might be an extreme difference of 30 seconds in the times of occurrence of the S.C. on the earth, the propagation being apparently from east to west on one hemisphere and from west to east on the other.

Fr. Rodés, who appeared to be unaware of the previous Papers by Angenheister, Chapman and myself, refers first to several more recent S.C.s, the times of occurrence of which at Tortosa he had compared with times supplied him for other stations. In some cases he mentioned "It would seem probable that . . . the results would indicate a simultaneous beginning all over the earth." "There are, nevertheless," he added, "some cases in which a propagation is strongly suspected" (l.c., p. 162). To account for these he advanced a theory which agrees with Prof. Chapman's in supposing the S.C. due to the immersion of the earth in a cloud of electric particles. But he did not think it possible "that a cloud at a distance of 150 million kilometers in free space has an effective transversal velocity greater than 2 kilometers per second caused by the solar rotation." He adds: "A rough approximation of the time required for the earth to become involved in the cloud can be easily obtained from its orbital velocity; this amounts to about six and a half minutes. . . . . It may be that when half, or even a greater part of the earth, is immersed

---

* "Nachrichten der K. Gesell. der Wiss. zu Göttingen Math. Phys. Klasse" (1913).

† Proc. Phys. Soc., Vol. 26, p. 137.

‡ Proc. Phys. Soc., Vol. 30, p. 205.

§ "Terrestrial Magnetism," Vol. 27, p. 161.

|| "Terrestrial Magnetism," Vol. 30, p. 45.

in the electric cloud, induction phenomena are produced which advance the time of beginning at other stations."

This theory would make the S.C. start at a point diametrically opposite that given by Chapman's theory, and travel in an opposite direction with a much slower velocity. The fact that both theories indicate where the earliest occurrence is to be looked for is, from the critical standpoint, a great advantage.

Fr. Rodés examined in the light of his theory the unrevised data for the Coast and Geodetic Observatory times of the fifteen S.C.s during 1906 to 1909, as well as a variety of data for more recent S.C.s, and he considered apparently that the results were rather favourable to his theory.

§ 3.

In the recent Paper by Messrs. Bauer and Peters the conclusions reached as to the easterly or westerly propagation of S.C.s at the rate required by Dr. Bauer's original theory seem to be in practical agreement with the conclusions reached by Prof. Angenheister and myself, but there is no clear explicit statement on the subject. This is the more to be regretted owing to the doubts thrown on the data which we employed. After referring to the revision of the Coast and Geodetic Observatory data mentioned above, they say (l.c., pp. 49 and 50) " the revised data were published in 'Terrestrial Magnetism,' Vol. 16, pp. 200-204, 1911. It had been the intention to follow the same procedure for other observatories in order that a discussion might be based on strictly homogeneous data; however, various matters operated to frustrate this plan. In the meantime, discussions of the published data for the 15 cases were undertaken and published by Dr. G. Angenheister and by Dr. C. Chree. *In neither case was any attempt made to use only strictly homogeneous data.* As a group, the time scalings for the four observatories in England differed more amongst themselves than those for any other similar group, as, for example, the one composed of the observatories in India and Burma. The observatories in England showed ranges, which in a number of cases amounted to from 4 to 6 minutes of time (in the case of disturbance 13*a* the *Z*-times at Greenwich and Falmouth differed by 10 minutes from one another). . . . So also Angenheister failed to note in his publication that in the case of disturbance No. 3*a* (December 21, 1906), for example, his times of beginning of the disturbance at Samoa Observatory (Apia), both for declination and horizontal intensity, . . . were systematically about 3 minutes less than the corresponding times at the Potsdam Observatory. . . ." The failure of Prof. Chapman and Fr. Rodés to employ " strictly homogeneous data " is also commented on.

§ 4.

As regards Prof. Angenheister, it may be pointed out that, since Samoa and Potsdam differ in longitude by about 175°, the phenomenon now commented on so unfavourably by Bauer and Peters would have been eminently reasonable if Dr. Bauer's original theory had been correct. As regards my own alleged shortcomings, it may be pointed out that I explicitly stated the belief that the differences in the times recorded were mainly at least of instrumental or observational origin. There was thus no more reason for me to concern myself about the differences between the four English stations (for three of which I had no responsibility) than about the differences between any other four stations near to or remote from one another.

As a matter of fact, Uccle, Val Joyeux, Tortosa and Pola, stations representative of S.W. Europe, will be found to exhibit at least as much diversity. As regards the case of S.C. No. 13, particularised by Bauer and Peters, the extreme differences from the mean time were exhibited, not by Falmouth and Greenwich, but by Falmouth (−7·4 m.) and Val Joyeux (+6·0 m.). I had explicitly called attention to this case in the following words (l.c., p. 142): "The Falmouth and Val Joyeux estimates for disturbance No. 13 appear abnormal, but were retained as they roughly neutralise one another in the mean." The method employed in my Paper—which has also been used a good deal by Bauer and Peters—was to calculate a mean time for each S.C. from the times recorded at all the stations, and use the difference of individual stations times from this in the discussion. Eighteen stations had supplied V-times ($V=Z$) for S.C. No. 13. Thus the retention or the omission of *both* Falmouth and Val Joyeux would not affect the mean time by as much as 0·1 m. Further, in any grouping of stations, Falmouth and Val Joyeux, owing to their geographical proximity, would naturally come in the same group, and the suspected data would again largely neutralise one another. In various other cases, as stated on my p. 140, I did omit suspicious data, excluding, in fact, all data from one station.

Prof. Chapman, for his part, as explained on his p. 209, omitted all times which differed as much as 2 minutes from the mean. Thus the charge of exhibiting an uncritical attitude to the data—data which, it should be remembered, had been published by Dr. Bauer himself—can hardly be fairly urged against either Prof. Chapman or me.

§ 5.

I am far from denying that greater consistency might have been obtained if all the curves had been re-measured by some one person with guidance obtained from the Potsdam curves. But it would have been difficult under such circumstances to secure perfect impartiality in the results. The fact that the data did not suffer sensibly from want of revision, so far as the immediate object in view was concerned, seems fairly obvious when we compare the mean times which I found for the several S.C.s with those now given as derived from the "homogeneous" data at Potsdam and the five Coast and Geodetic Stations (Sitka, Baldwin, Cheltenham, Vieques and Honolulu). Bauer and Peters give mean times separately, as I did, for the three elements declination (D), horizontal force (H) and vertical force (Z or V). Angenheister and Chapman confined themselves to H. Besides giving separate times for the three elements, Bauer and Peters give a composite mean time which allows weights of 3 to H, 2 to D and 1 to V. These weights are not unfairly representative of the relative importance of the elements, and this composite mean, though certain objections can be urged against it as a physical quantity, affords at least a convenient basis for comparing my mean times with those of Bauer and Peters. Calculating from my data 3-element mean times after the fashion of Bauer and Peters, the resulting times for the 15 S.C.s (algebraically) exceed those now given by Bauer and Peters by the following individual amounts: +0·4 m., −0·3 m., +0·3 m., +0·2 m., +0·2 m., +0·2 m., +0·5 m., −0·3 m., −0·1 m., −0·1 m., −0·3 m., +0·2 m., −0·3 m., −0·6 m., −0·2 m. The mean of these fifteen excesses is −0·01 m., showing that the differences may be treated as accidental. In only one case, No. 14, does my time differ by more than 0·5 m. from that of Bauer and Peters. On that occasion there is a difference of 1·2 m. between the times derived by Bauer and Peters from the D and H curve measurements, the difference in my case being 0·6 m.

§ 6.

As was pointed out in my original Paper, the differences between the times of S.C.s derived from the D, H and V curves on an individual occasion, though containing a large accidental element, are partly of a systematic character. At the average station there is a decided tendency for the D time to be earlier than the V, and the H time earlier than the D. As shown in my Table V (l.c., p. 147), the means of these time differences for the 15 S.C.s, allowing equal weight to each station, irrespective of the number of data it supplied, were $D-H=+0{\cdot}24$ m., and $V-H=+0{\cdot}65$ m. This phenomenon cannot be assigned to the lack of "homogeneity" in my data, as it is clearly apparent in the data in Bauer and Peters' Table III (l.c., p. 53). For the testing of Dr. Bauer's original theory, or that of Fr. Rodés, which postulates a similar comparatively slow rate of propagation, the above phenomenon is unimportant.

But it is otherwise when we have to do with theories such as Chapman's, which postulate a much higher rate of propagation. The question thus demands further consideration.

An S.C. is neither infinitely large nor infinitely rapid. Also a change of curve ordinate to be perceptible must attain a certain size. Thus some interval, whether a fraction of a second, a few seconds, or a number of seconds, must elapse before an S.C. movement on a magnetic curve is recognisable. The time will naturally be shorter the larger the component of the disturbing force affecting the particular magnetograph, and the more sensitive the magnetograph. A good idea of the general character of S.C.s at different parts of the earth may be obtained from plates XIX to XXVII of the volume "Terrestrial Magnetism, British Antarctic Expedition," 1910-13. The traces of three elements are shown, and the corresponding scale values are indicated by the length of the arrows drawn adjacent to the curves, each representing 50γ. In some cases N (north component) and E (east component) are shown instead of H and D, but there is usually a close resemblance between N and H changes. It is at once obvious that the change in H is usually much the largest, especially in low latitudes. In a D magnetograph the equivalent in force of 1′ varies directly as the local value of H. In ordinary magnetographs 1 mm. of ordinate represents roughly 1′. Thus, as measurers of force, D magnetographs are apt to be insensitive instruments near the magnetic equator, where H is large. The short length of the arrows representing 50γ in the case of the Alibag (Bombay) and Honolulu D curves in the plates referred to above at once catches the eye. These considerations might explain a small lag in the times derived from the D and V curves, as compared with those derived from the H curves, but they certainly do not account for all the phenomena observed. It is true that the D-H difference is specially prominent in the "homogeneous" data from those two of Bauer and Peters' stations, where H is highest, being $+0{\cdot}83$ m. at Honolulu and $+0{\cdot}58$ m. at Vieques. But Bombay is a station with a still higher value of H, and for it I got D-$H=-0{\cdot}19$ m. If, moreover, we regard a station as good or bad according as the times assigned at it differed little or much from the mean of the times assigned at all the stations, Bombay was better than the average. A positive value for D-H may be, of course, a purely natural phenomenon, the disturbing force having initially no horizontal component perpendicular to the magnetic meridian. But it is difficult to believe that this could be a general phenomenon, in view of the continual secular change and other considerations. If it were a natural phenomenon, we should at least expect similar results at stations in the same part of the world. While, however, *D-H* at Uccle on an average from 13 S.C.s was +0·42 m., at Wilhelmshaven, on an average from 12 S.C.s, it was −0·71 m. At one non-British station, which need not be specified, the mean value of *D-H* was +3·05 m., no one pifference exceeding +5·6 m. In such a case one would think there must be some deculiarity in the way of marking or measuring the times.

§ 7.

As regards a difference between the *V* and *H* times, a total absence of a vertical component at the start seems *a priori* a much less unlikely contingency than a total absence of a *D* component. *V* might again alter initially as the square of the time, while *H* altered as the first power. On the other hand, an instrumental lag of a frictional kind in the ordinary Lloyd-balance *V* magnetograph is not at all an unlikely contingency. I am afraid the *V* phenomena during S.C.s are unlikely to be satisfactorily ascertained until use is made of a horizontal coil and galvanometer, such as Dr. Crichton Mitchell* has employed at Eskdalemuir. However this may be, the fact remains that when a mean value of *V-H* was calculated for each of the 15 S.C.s, from all the stations available, a plus value was obtained for every S.C., except No. 1, for which the result was zero. When the stations were considered individually, all the S.C.s available being utilised, a negative value was obtained for two or three stations which had supplied data for only a few S.C.s ; but of the stations which had supplied data for a majority of the S.C.s only one (Bombay) gave a negative value, and as it was only −0·04 m. it hardly counts. As in the case of *D-H*, there were a few stations at which the phenomenon could hardly be explained by anything but some peculiarity in marking or measuring times. In one such case, again a non-British station, the mean value obtained for *V-H* from 13 S.C.s. was +3·25 m., all the differences being positive and none exceeding +4·8 m.

§ 8.

The values of the $D \sim H$ and $V \sim H$ time differences for the "homogeneous" data employed by Bauer and Peters are naturally of special interest, because they must inevitably influence our attitude to Bauer and Peters' conclusions. These differences are given in the following table, the stations being arranged in order of geographical latitude.

TABLE I.—*Differences in Mean Times for D, H and V.*

Mean time difference.	Sitka.	Potsdam.	Baldwin.	Cheltenham.	Honolulu.	Vieques.
	m	*m*	*m*	*m*	*m*	*m*
D—H	+0·04	+0·01	+0·19	+0·07	+0·83	+0·58
V—H	+0·27	+0·89	+0·30	+0·17	+0·52	+0·32

It will be observed that the value of *V-H* at Potsdam is decidedly in excess of the mean derived in my Table V (l.c., p. 147) from all the stations available. The other values, except those for *D-H* at Honolulu and Vieques, are smaller than those at the average station. It is obvious, however, that they might be rather vital when it comes to testing Chapman's theory, or any theory depending on similarly small time intervals.

---

* Proc. Roy. Soc. of Edinburgh, Vol. 45, p. 297.

§ 9.

After giving the *D*, *H* and *V* times of the 15 S.C.s at their 6 selected stations, and a variety of statistical deductions therefrom, Bauer and Peters proceed to a discussion of Fr. Rodés' theory. They conclude that the phenomena are not compatible with at all as slow a rate of propagation as this theory requires. Then, after a mere reference to Prof. Chapman's theory, they proceed in their § 22 to test the hypothesis that S.C.s more often travel easterly than westerly, and conclude that "The average speed of propagation . . . would apparently be about 1,000 km. per second eastwardly." In their § 23 they then try the hypothesis that the direction of propagation is towards the west, and on this hypothesis find that " the apparent speed of westwardly propagation is about 800 km. per second." In their § 24 the authors proceed to say " But thus far we are unable to determine definitely in which direction, on the average, the abrupt disturbances (their name for S.C.s) are actually propagated. . . . Finally the desired clue was obtained by computing the mean magnetic latitudes of each group [they had arranged the 6 stations in groups of 3 or 2] . . . whether we grouped the observatories according to increasing east longitude, or according to increasing west longitude, in either case the magnetic latitude was increased in going from the first to the second group [i.e., from the group giving the earlier to that giving the later mean time for the S.C.s]. A preliminary examination indicates that this fact was the chief cause for the conclusion reached in 1910 " (already given above). A discussion of the hypothesis that S.C.s "progress generally according to increasing magnetic latitude" follows in their § 25.

§ 10.

Before discussing the results further, the use of the term " magnetic latitude " requires explanation. Bauer and Peters' magnetic latitude φ' is really defined as $\varphi'=\tan^{-1}(\frac{1}{2}\tan I)$, where *I* is the true dip. The term has a precise physical significance in the case of a uniformly magnetised sphere. If $\varphi=\pi/2$ represents the magnetic axis of such a sphere, it is easily proved that

$$\tan I=2\tan\varphi.$$

As is well known, the first order terms in the Gaussian analysis of the earth's magnetic potential are much the largest, and the earth's magnetism, so far as expressed in these terms, is the same as that of a uniformly magnetised sphere whose axis is inclined to the axis of rotation (geographical axis) at some 12°, the northern end of this axis being not far from 70°*W*. It is not unusual to speak of the axis of the first order Gaussian terms as the earth's magnetic axis, etc. When this is done, we naturally think of lines of equal magnetic latitude as small circles on the earth's surface, having their centres on the magnetic axis, and otherwise analogous in every way to lines of geographical latitude. But the first Gaussian harmonic supplies only a first approximation to the earth's real magnetism, and it is a somewhat rough approximation when it comes to the question of the true position of the magnetic poles, defined as the places where the dipping needle is vertical. If we define φ′ as Bauer and Peters do, we must take the earth's true isoclinals as lines of equal magnetic latitude. The complications that ensue will be obvious to anyone who considers even the smoothed isoclinals which do duty on world charts. The geographical distance between two given isoclinals is a very variable quantity at different parts of the earth's surface. If the time of passage of an S.C. from one isoclinal to another is invariable—as is implied by Bauer and Peters' calculations on their pp. 59-61—the real velocity of propagation must be very variable. When we pass to true isoclinals there are often large local irregularities. There are even in places small complete ovals. Thus, if we had transmission strictly following the direction of increasing dip, we should in some adjacent regions not near the equator have propagation in diametrically opposite directions.

§ 11.

The results which appear much the most favourable to this final hypothesis of Bauer and Peters are those given in their Table XI (l.c., p. 59), as derived from the *H* times of the 15 S.C.s at their six stations. These are given below in Table II. δT means the departure of the time given by the individual station from the mean of the times at all six stations. The information as to the geographical co-ordinates has been added to give an idea of the zig-zag nature of the motion which is suggested by the values of δT, if accepted as physical facts.

TABLE II.

Station.	Lat. *N.*	Long. *W.*	φ'	δT
	°	°	°	*m*
Honolulu	21·3	158·1	22·7	−0·74
Vieques	18·1	65·4	30·4	−0·27
Potsdam	52·4	346·9	48·7	+0·05
Baldwin	38·8	95·2	52·2	+0·12
Cheltenham	38·7	76·8	54·7	+0·14
Sitka	57·0	135·3	61·2	+0·67

The formula $\delta T = x\delta\varphi'$, with x the velocity per 1° of φ', applied to the data in Table II by Bauer and Peters, is said to show a correlation coefficient of 0·96.

In a second investigation the authors employed the less homogeneous results of all the (29) observatories arranged in eight groups according to magnetic latitude. In this case *V* supplied the results most favourable to the hypothesis. Stations with southerly dip appear in the same group as stations with corresponding northerly dip, in strict accordance with the view that the direction of propagation is from the (magnetic) equator towards either pole. In both these investigations the times derived from *D* gave very poor support to the theory. Some *H* data were also considered from an additional 15 S.C.s recorded in 1922 to 1925. On their p. 67 the authors summarise their results as follows :

"§ 34. Such evidence as could be obtained from the data at the observatories chiefly considered in this Paper (suggest that ?) the speed of progression of an abrupt disturbance (i.e., an S.C.) around the earth may be 1,000 kilometres per second, or more. The average speed of progression in magnetic latitude, from the combined testimony of the 30 disturbances, would be about 100 kilometres per second, so that if an abrupt disturbance progressed uninterruptedly from the magnetic equator to the magnetic pole it would take about 1·8 minutes. There may also be cases in which an abrupt disturbance will occur everywhere simaltaneously in so far as can be determined with the instrumental appliances in general use. § 35. We regard at present the foregoing ideas chiefly as a working hypothesis to be tested with the aid of additional material. . . . ."

§ 12.

It may be noted that an equatorial velocity of 1,000 km. per second would give about 40 secs. for the circumnavigation of the earth. As this seems the lowest velocity now claimed for east⁓west propagation, we may presumably regard Dr. Bauer's original view that S.C.s perambulated the globe in from 3 to 7 minutes as definitely abandoned. But this seems the only definite result reached.

If the true interpretation of the " working hypothesis " is that an S.C. originates simultaneously everywhere in the magnetic equator, and thence travels towards both true magnetic poles, this would imply in the North Atlantic and in Western Europe a geographically western component, and in the southern Atlantic an easterly component. In a large part, however, of Asia, Eastern Africa and Eastern Europe the direction of propagation would be nearly in the geographical meridian, and in most areas there would be a considerable component in that direction. It would thus appear worth while considering what conclusions I drew from my original investigation into the possibility of a north-south direction of propagation, though it is not referred to by Bauer and Peters. It is true that I assumed that the direction of propagation was the same and not opposite in the northern and southern hemispheres. But this could not make much difference to the result, as only three of the stations I employed had southerly dip, and they were all in low latitudes. The following is the conclusion I drew for *H* from the data of 30 stations (l.c., p. 141): " So far as *H* is concerned, there seems no more evidence of motion of disturbances (S.C.s) along meridians than there was along parallels of latitude." In the case of *V* only 26 stations were available, and some of these gave data for a minority of the S.C.s. The conclusion drawn (l.c., p. 142) was as follows: " In disturbance No. 1 there is a suggestion of motion from south to north, the first seven entries (station differences from mean time, the stations being arranged according to decreasing northern latitude) being all plus and the last six all negative. The numerically largest values, however, both positive and negative, occur in intermediate latitudes, and the phenomenon may be quite accidental."

§ 13.

In view of Bauer and Peters' conclusions, especially their suggestion of oppositely directed propagation in the two hemispheres, I have looked at the data again, and give in Tables III and IV some data which appear to throw some further light on the subject.

Table III reproduces some of the results I had obtained for the differences between mean times for *H*, *D* and *V* at the individual stations, and at all the available stations combined. The last column, containing a combined mean which allows weights of 3 to *H*, 2 to *D* and 1 to *V*, is new. The data assigned to those of Bauer and Peters' stations included differ slightly from those deducible from Bauer and Peters' own figures, because my all-station means differ from theirs.

TABLE III.—*Individual Station Time Differences.*

Station.	Latitude.		Difference from Mean-station time (minutes).			
	Geog. °	Mag. °	*H*	*D*	*V*	3 elements.
Sitka	57 N	61 N	+0·73	+0·48	+0·27	+0·57
Ekaterinburg	57 ,,	55 ,,	+0·78	+0·65	+1·08	+0·79
Stonyhurst	54 ,,	52 ,,	−0·74	−0·77	−1·00	−0·79
Wilhelmshaven	54 ,,	51 ,,	−0·34	−1·21	...	−0·69
Potsdam	52 ,,	49 ,,	+0·11	−0·12	+0·35	+0·07
Greenwich	51 ,,	50 ,,	+0·47	+0·36	+0·12	+0·37
Helwan	30 ,,	23 ,,	+0·03	+0·84	+0·59	+0·39
Honolulu	21 ,,	23 ,,	−0·68	−0·09	−0·81	−0·50
Bombay	19 ,,	11 ,,	−0·24	−0·67	−0·93	−0·50
Vieques	18 ,,	31 ,,	+0·11	+0·55	+0·13	+0·26
Kodaikanal	10 ,,	2 ,,	+0·81	−0·25	+0·24	+0·36
Buitenzorg	7 S	17 S	−0·25	−0·55	−0·76	−0·43
Samoa	14 ,,	16 ,,	−0·18	−0·30	+0·85	−0·05

It will be obvious to any mathematician on inspection of Table II that the conclusion drawn by Bauer and Peters from the *H* data, as to the motion from south to north magnetic in the northern hemisphere depends mainly on the two stations of extreme magnetic latitude, Sitka and Honolulu. On looking at Table III it will be seen how peculiarly favourable to the theory the choice of these two stations happened to be. Ekaterinburg, it is true, might have been as favourable as Sitka, and Bombay in the case of *V* and *D*, though not in the case of *H*, as favourable as Honolulu. Also Greenwich might have been as favourable as Potsdam. But the substitution of Stonyhurst or Wilhelmshaven for Sitka, and of Kodaikanal or Helwan for Honolulu would have made all the difference in the world to the results. In the case of *V* the opposition presented by Buitenzorg and Samoa is most striking. We might, in fact, select six stations which would lead to results diametrically opposed to those of Bauer and Peters.

§ 14.

Inspection of my Table VII (l.c., p. 151) did, however, suggest that if we concede the possibility of propagation along geographical meridians, or along curves orthogonal to isoclinals, more is to be said for propagation to the north than for propagation to the south in the northern hemisphere. The stations were divided into two groups, according as the station time was earlier or later than the all-station mean time. This was done for *H*, *D* and *V* separately. The results are given in Table IV, magnetic latitude having the meaning assigned it by Bauer and Peters. When either group of stations contained a station or stations having southerly latitude, two mean latitudes were calculated, the one arithmetical (unbracketed), the other algebraic (bracketed). The former figure should be employed in connexion with Bauer and Peters' hypothesis. The latter gives velocity the same direction S. or N. everywhere. A difference between the mean latitudes found for the two groups of stations is favourable to a finite rate of propagation, the result being the more favourable the larger the difference between the two mean latitudes. The results, it will be seen, are all favourable to propagation from the magnetic equator or from south to north in the northern hemisphere. The difference figures in brackets for the two mean latitudes are in excess of the unbracketed. This is at least not unfavourable to the view that the velocity has the same direction in the two hemispheres.

Whether we take geographical or magnetic latitude, the element the results from which appear most favourable to the hypothesis of propagation with a finite velocity is V, and as we have already observed it is the element instrumentally most open to suspicion. Even in the case of V the results do not really afford much support to Bauer and Peters' theory. If 90° in latitude were really covered in 1·8 m., we should expect a much greater difference between the mean latitudes from the two groups of stations in view of the large differences between the corresponding mean times.

TABLE IV.—*Mean Latitudes of Groups of Earlier and Later Stations.*

Group of stations.	Mean geographical latitude.			Mean magnetic latitude.		
	H	*D*	*V*	*H*	*D*	*V*
	° °	° °	° °	° °	° °	° °
Earlier...	36·0(28·1)	36·7(29·8)	30·0(23·6)	33·5(26·3)	33·7(27·5)	27·5(22·3)
Later	39·7	39·4	41·9(39·9)	40·4	41·3	41·9(39·6)
Latitude difference ...	3·7(11·6)	2·7 (9·6)	11·9(13·3)	6·9(14·1)	7·6(13·8)	14·4(17·3)
Time difference	0·85 m.	0·82 m.	1·43 m.	0·85 m.	0·82 m.	1·43 m.

§ 15.

A theory which suggests propagation from the equator to the poles is much more difficult to test satisfactorily than one which suggests propagation completely round the earth, or from one end of an equatorial diameter to the other. There are, in the first place, only 90° from equator to pole (geographical or magnetic). Then there are few magnetic observatories in either equatorial or high latitudes. Of the 30 observatories included in my Paper only one had a magnetic latitude less than 10°, and only three had magnetic latitudes greater than 55°. Bauer and Peters' six observatories gave a range of magnetic latitude of only 38·5°.

To test satisfactorily a rate of propagation from the equator such as 90° in 1·8 m. by means of records from existing observatories obviously calls for higher time accuracy than suffices to test either Dr. Bauer's original theory or that of Fr. Rodés. This is all the more true because—as the Antarctic volume referred to above clearly shows—S.C.s change their type with magnetic latitude. At stations like Bombay, Mauritius or Helwan, in lower latitudes, the H movement, which is far the most important, seems normally to be unidirectional (an increase of H); whereas in higher latitudes—e.g., at Eskdalemuir or Sitka—it is generally, if not always, oscillatory. Again, curves in higher latitudes are much more subject than those in lower latitudes to irregular small oscillations, and the presence of these may make it difficult, if not impossible, to say exactly what the S.C. movement has consisted of.

Another consideration is that Bauer and Peters' latest hypothesis may easily undergo transformation. The idea of a disturbance propagated from the equator to both poles may recommend itself to those who suppose, with Prof. Störmer and Dr. Van Bemmelen, that a ring of ions in the upper atmosphere over the magnetic equator is responsible for some of the phenomena of magnetic storms. But, obviously, others might think the S.C. more likely to originate in one or in both auroral zones. We might thus have variants of the theory, some postulating movement invariably to or from the magnetic equator, others postulating the same direction of motion whether north or south all the way between the auroral zones. If, moreover, a velocity as low as 90° in 1·8 m. proved untenable, an enhanced velocity might be suggested.

§ 16.

My principal reason for discussing the matter at such length now is that, at the last meeting of the International Union of Geodesy and Geophysics, a sum of money was voted to the Section of Terrestrial Magnetism and Electricity for the purpose of installing at a few stations special apparatus for ascertaining whether S.C.s do or do not undergo propagation at a finite rate. It will, I think, be generally agreed that, whatever theory or theories there may be to test, the same magnetic element or elements should be recorded at the special stations. Financial considerations may require a single element to be selected, and an early decision on that point may be necessary. The stations most suitable for the purpose have also to be considered.

For ordinary purposes the *D* magnetograph has much to recommend it. It is the simplest to construct. Its scale value is invariable, and there is no temperature coefficient. On the other hand, for this particular enquiry the *H* magnetograph has special advantages. It is easier to determine accurately the commencing time of a large than of a small movement, and in the case of S.C.s the *H* movement is usually much the largest. Again, as explained above, whatever the reason, the commencing times found for S.C.s from the *H* curves tend to be earlier than those derived from the *D* or *V* curves. Thus we should naturally feel more confident of having timed the real commencement if we used an *H* magnetograph than if we used a *D* or a *V* magnetograph. To test any theory such as Bauer's original theory, or those of Chapman and Rodés, in which the direction of propagation is approximately east and west, it is obviously desirable, if an *H* magnetograph is used, to select stations in which the *H* S.C. movement is of a common type. This suggests that the stations should be in a comparatively low latitude. A comparison of records from a number of possible stations would be a desirable preliminary to a final selection of stations. Bauer's original theory may require no further testing, but there remain Chapman's and any number of possible intermediates between it and Rodés' theory.

It would seem desirable to deal thoroughly first with east-west propagation. The test of south-north propagation promises to be a more difficult job, and it would be well in any case to allow further time for the criticism of Bauer and Peters' last theory or for the proposal of modifications of it.

Local characteristics seem to play a greater part in the vertical component than in the horizontal components during ordinary magnetic disturbance, and the same may be true even for S.C.s. Thus an investigation of the *H* phenomena *may* not exhaust the subject. But in the case of the ordinary *V* magnetograph it is difficult to feel sure that the record of rapid changes of force is free from instrumental peculiarities, and it might be well to await the development of instruments employing a horizontal coil and a galvanometer.

DISCUSSION.

Mr. F. E. Smith said that the expression "homogeneous data" appears to mean the same as "arbitrarily selected data," and physicists are indebted to the author for his strenuous insistence on a rigorously scientific examination of the theories that have been put forward. The type of apparatus required for settling the questions at issue would depend on the theory to be tested. A theory which postulates a comparatively slow rate of propagation of the sudden commencements could very easily be tested with the aid of wireless time signals, but if the time differences between the sudden commencements at different stations be very small, the problem becomes much more difficult.

VI.—THE MEASUREMENT OF TEMPERATURE BY THERMOCOUPLES IN UNEQUALLY HEATED ENCLOSURES.

By W. MANDELL, *B.Sc.*, Assistant Lecturer in Physics, University College of Wales, Aberystwyth.

Received July 7, 1925.

(*Communicated by* PROF. GWILYM OWEN.)

ABSTRACT.

In measuring temperature by thermocouples in unequally heated enclosures it is shown that the recorded temperature depends upon the thickness of the couple, the nature of the walls of the enclosure and the nature of the gas. An explanation is suggested based upon the fact that the amount of radiation received and emitted by a couple depends upon its position in the enclosure, and that the amount of energy transferred to it by molecular impact varies with the nature of the gas.

INTRODUCTION.

IN a Paper on "The Temperature Gradient in Gases at Various Pressures," Mandell and West,* using a chamber consisting essentially of two large horizontal, parallel plates, the upper plate being kept at a constant high temperature, whilst the lower was kept cool, showed that with two thermocouples of different diameters there was a small, but definite and systematic, difference in the temperatures recorded by them in air at atmospheric pressure. Two comparatively thick couples (diameters 0·0126 and 0·0209 cm.) were used and, for a temperature difference of 130°C. between the two plates, the readings of the couples varied by about $\pm 1\frac{1}{5}$°C. Henderson† using a single couple showed that the recorded temperature appeared to be too low near the hot plate and too high near the cold plate and attributed this to a radiation effect.

The experiments described in the present Paper were devised to investigate this interesting phenomenon of different recorded temperatures by different couples. It was thought that by using couples varying considerably in thickness, and with a much larger temperature gradient in the gas, the effect would be increased. The experiment therefore resolved itself into determining as accurately as possible the difference in temperature recorded by thermocouples when placed side by side in the same horizontal plane in the gas. It was also thought possible that the nature of the gas and the nature of the surfaces of the enclosure might have some influence on the results.

If the temperature differences varied in a uniform manner with the thickness of the couples, it was sought to find how they differed in temperature from a couple of zero diameter by a method of extrapolation first suggested by Kreisinger and Barkley.‡ As will be seen later, the results reveal the interesting and important facts that in an unequally heated enclosure in which convection is eliminated, the temperature recorded by a thermocouple depends upon its thickness, the nature —bright or black—of the walls of the enclosure, and also upon the nature of the gas in which it is placed.

---

* Proc. Phys. Soc., Vol. 37, p. 20 (1924).

† Phys. Review, Vol. 50, p. 26 (1920).

‡ Bull. U.S. Bureau of Mines, 145 (1918). Kreisinger and Barkley measured the temperature of a stream of air flowing through different types of boilers.

APPARATUS.

The apparatus used was practically the same as in the previous Paper,* excepting that the sides of the chamber consisted of a glass cylinder 1·95 cm. long. It will be seen, therefore, that we have in effect a layer of gas some 2 cm. thick enclosed between two horizontal plates—under conditions in which convection, and the influence of the sides on the main body of the gas may be assumed negligible, and in which the lines of flow of heat, at any rate, through the central portion of the layers, may be assumed vertical.

A movable, horizontal, porcelain platform was used as before, and now carried four thermocouples of different diameters.

PREPARATION AND CALIBRATION OF THE THERMOCOUPLES.

The thermocouples were of copper and constantan and for convenience are denoted by the terms (α, very thin, diam. 0·0014 cm.), (β, thin, 0·0123 cm.), (γ, thick, 0·0195 cm.) and (δ, very thick, 0·0315 cm.).

They were made by fusing the wires together "end-on" in a reducing flame. Several hundred couples were made until specimens were obtained showing no blob at the junctions when examined under a microscope. When fixed their general appearance was that of four almost coplanar parallel cylinders of equal lengths. The couples were placed on the platform in the order δ, β, γ, α, that is, not in the same order as their thickness, the distance between the two outside couples being 1·2 cm.

In regard to the couples on the hot and cold plates, a convenient method had to be devised so that they could be detached easily for re-calibration without unsoldering them, as this might alter their e.m.f.s. Small, thin, circular-brass discs of about 1 cm. diameter and of the same material as the hot and cold plates were employed. The couples were "hard-soldered" on to the brass discs, which were then screwed into holes in the hot and cold plates at a distance of about 1·5 cm. from their centres until the surfaces of the brass discs were level with the plane experimental surfaces.

Since the *differences* of temperature to be measured were only of the order of a few degrees, all the couples had to be very carefully calibrated and an accurate method of reading to $\frac{1}{10}$°C. had to be devised.

Before the six couples were actually fixed in the apparatus they were calibrated in an electrically heated black-body enclosure against a mercury-in-glass thermometer. It was found that on keeping them at a temperature of 160°C. there was a gradual change in their e.m.f.s for about 20 hours. The actual calibration was not begun until after heating for about 50 hours. The e.m.f.s of all the couples were then read for 28 different temperatures, a considerable time having to elapse between each set of readings, until the temperature was absolutely steady.

---

* Loc. cit.

As was to be expected, for any fixed temperature, the e.m.f.s of the couples were not quite the same and, in fact, were found to be in the decreasing order *α*, *γ*, *δ*, *β*. A graph of such large dimensions was required that it was considered that the readings for 28 different temperatures were not sufficient, so the following method of graphing was employed. The temperatures of the enclosure were plotted as abscissæ and the *differences* of e.m.f. between the very thin couple and the other platform couples were plotted as ordinates, the result giving three parabolas. With the help of this graph the proper e.m.f.-temperature graph for all the couples could be constructed after drawing the smooth curve through the 28 points for the very thin couple. It follows that this method was especially accurate for the measurement of small temperature differences. The couples were recalibrated after using for six months and at other times, and had not changed to any measurable extent.

METHOD OF CARRYING OUT AN EXPERIMENT.

The apparatus was filled with the dry gas at atmospheric pressure. The hot and cold plates usually took three to four hours to attain the temperatures chosen, before steady conditions were obtained. The platform thermocouples which had previously been placed as close to the hot plate as possible were then gradually moved down by measured steps, until the cold plate was reached. At each step the e.m.f.s registered by all the thermocouples, including those on the hot and cold plates, were noted. These observations usually took one and a half to two hours, since for each movement of the platform it was necessary to await steady conditions.

RESULTS.

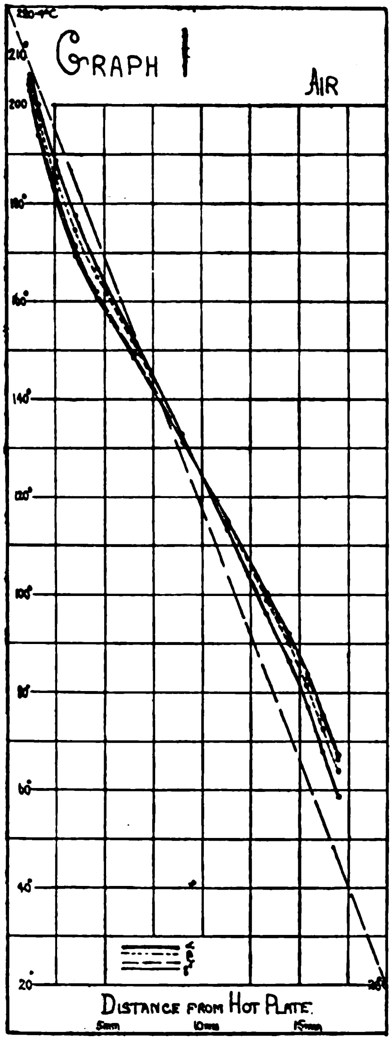
The first series of graphs records the results obtained with gases at atmospheric pressure, the hot and cold plates having highly polished brass surfaces. In this series of experiments the distance of nearest approach of the couples to the hot plate was 1·25 mm.

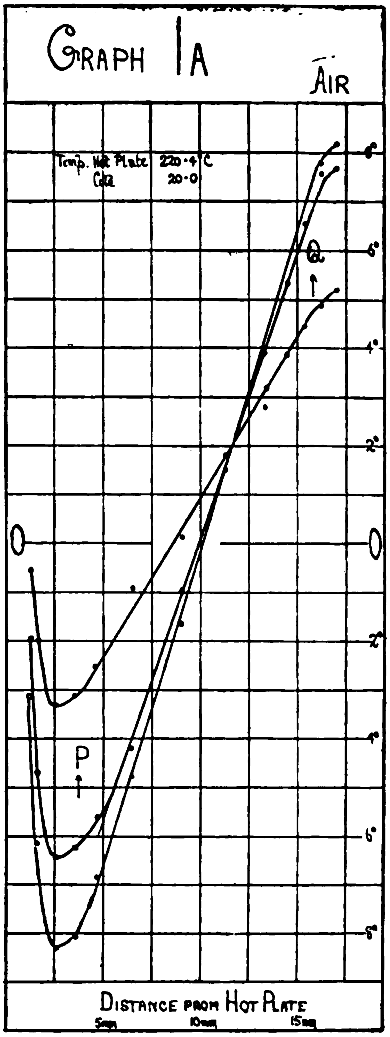
Graph 1 is typical of about twenty experiments obtained with air, and is constructed from the data of the first four columns of Table I. The hot plate was at a

TABLE I (*Graphs* 1 *and* 1A).

Brass Surfaces.		Air.	Atmospheric Pressure.	Temperature {Hot plate, 220·4°C. Cold plate, 20·0°C.			
α V. Thin.	*β* Thin.	γ Thick.	δ V. Thick.	Differences (°).			Distance in mm. from hot plate.
				α and *β*	*α* and γ	*α* and δ	
206·35	205·8	204·4	203·25	—0·55	—1·95	—3·1	1·25
200·00	198·0	195·3	193·85	—2·0	—4·7	—6·15	1·70
188·7	185·0	182·25	180·4	—3·3	—6·45	—8·3	2·60
177·5	174·4	171·35	169·4	—3·1	—6·25	—8·1	3·55
167·5	165·0	161·9	160·65	—2·5	—5·6	—6·85	4·65
153·3	152·4	149·1	148·5	—0·9	—4·2	—4·8	6·50
132·95	133·1	132·0	131·3	+0·15	—0·95	—1·65	9·10
113·45	115·3	115·25	114·9	+1·85	+1·8	+1·55	11·30
96·25	99·05	99·45	100·15	+2·8	+3·2	+3·9	13·30
86·5	90·4	91·85	91·9	+3·9	+5·35	+5·4	14·45
76·95	81·4	83·5	83·8	+4·45	+6·55	+6·85	15·35
67·5	72·4	75·1	75·3	+4·9	+7·6	+7·8	16·20
58·7	63·9	56·4	66·9	+5·2	+7·7	+8·2	17·00

temperature of 220·4°C., and the cold plate 20·0°C. The dotted straight line joining these temperatures would represent a uniform temperature distribution between the plates. The experimental curves, however, as can be seen, deviate markedly from such a line, and furthermore, the temperature distribution as recorded by the couples varies in a regular manner with the thickness of the couples. It will be seen that the thinnest couple reads the highest temperature near the hot plate and the lowest temperature near the cold plate.





Graph 1A is also drawn from Table I, where columns 5, 6 and 7 give the differences in temperature between the α and β, α amd γ and α and δ couples respectively. It is a simple method of representing clearly how the temperature differences of the couples of Graph 1 vary across the chamber. The ordinates from 0—0 represent the temperature differences in degrees between the very thin (*a*) and the other platform couples, the ordinate being drawn below 0—0 if the temperature be lower, and above, if higher than that of the thinnest couple. It will be noticed in this and similar graphs that three straight lines are obtained which bend sharply when a few millimetres from the hot and cold plates.

When a result similar to Graph 1A was first obtained showing, as it does, a difference of ±8°C. between the *a* and *δ* couples, it was thought that perhaps heat was being conducted from the wires, the thicker couples being, of course, the better conductors. On referring, however, to Fig. 1 it is seen that about seven centimetres of the thermocouple wires lie on each arm of the platform—that is, in the same horizontal plane where the temperature is uniform over a considerable area, so that there would be little tendency for loss of heat by this means. Besides, no explanation of the effects of conduction would account for the peculiar bend of the curves of temperature distribution in Graph 1, or the bends in the temperature difference curves of Graph 1A.

The next question to decide was whether these differences were due, in some ways to the order in which the couples were placed on the platform. At different times (owing to breakages) the couples were fixed in different order, but similar result, were always obtained.

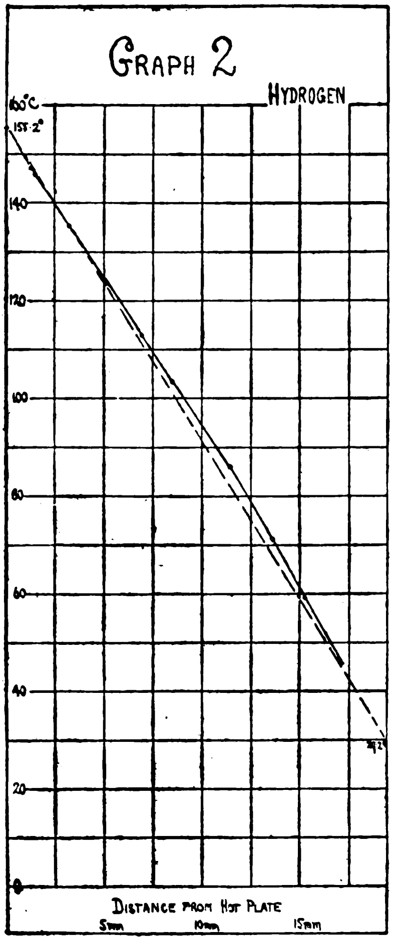
It is to be noted, too, that the differences recorded do not follow the natural variations in e.m.f. of the couples, which, as pointed out on page 49, take place at any constant temperature.

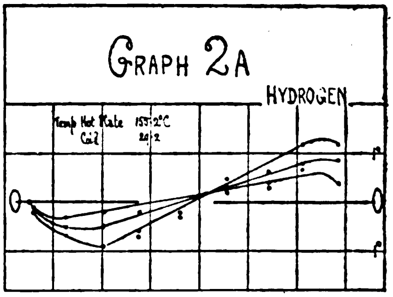
Any errors arising from movements of the platform by sagging due to time are ruled out by the fact that identical results were obtained with any particular gas after the apparatus had been used for several weeks as were obtained the first time the apparatus was used. Furthermore, readings taken with two very thin couples showed that the platform remained not only rigid, but also truly horizontal. Additional proof that the temperature differences recorded by the couples is an effect not to be attributed to conduction along the wires, nor to warping of the platform, is shown by the fact that different gases give different results.

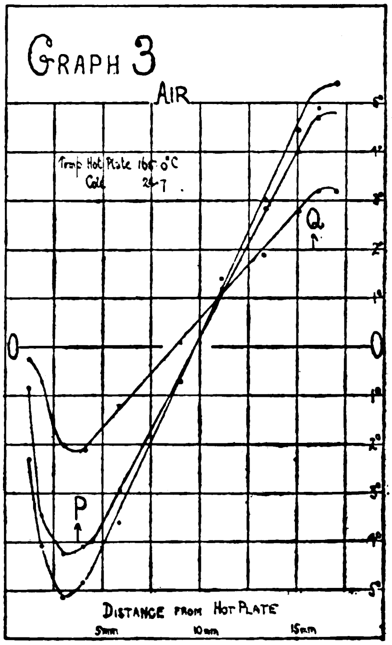
Graph 2 was obtained for the very thin couple when hydrogen from a gas cylinder replaced the air in the chamber, the temperatures of the hot and cold plates being 155·2°C. and 29·2°C. respectively. From this graph it is seen that there is scarcely any " dip " in the curve in front of the hot plate. The differences between the couples were so small that they cannot be represented conveniently on Graph 2, and are given on Graph 2A, which shows that the four couples in hydrogen record readings which do not vary by more than about ±1°C.

Graph 3 obtained with air, may be compared with Graph 2A for hydrogen. The differences in temperature between the plates in the two experiments were not the same, being 140·3° and 126·0°C. respectively, but this would not account for the striking differences in the results obtained with the two gases.

A series of readings was then taken with air at atmospheric pressure, the object being to see how the temperature differences between the couples varied with the temperature gradient in the gas, and by extrapolation, what would be the temperature recorded by a couple of zero diameter. The results obtained are shown in Graphs 1A, 3, 4, 5, 6, the differences in temperature between the hot and cold plates being respectively 200·4°, 140·3°, 166·7°, 99·6° and 62·7°C. A series of straight lines of different slopes was obtained. It will be seen that the measurement of the distances of the central axes of the couples relative to a horizontal plane, say, of the platform, must be measured very accurately. Any error in this measurement for a couple would displace one of the straight lines of the above graphs parallel to itself. Hence, since there may be a slight uncertainty as to the exact point where these lines cross, it is preferable to take the *total* temperature differences for the couples considered at two points P and Q on the straight lines 3·75 mm. from the plates.

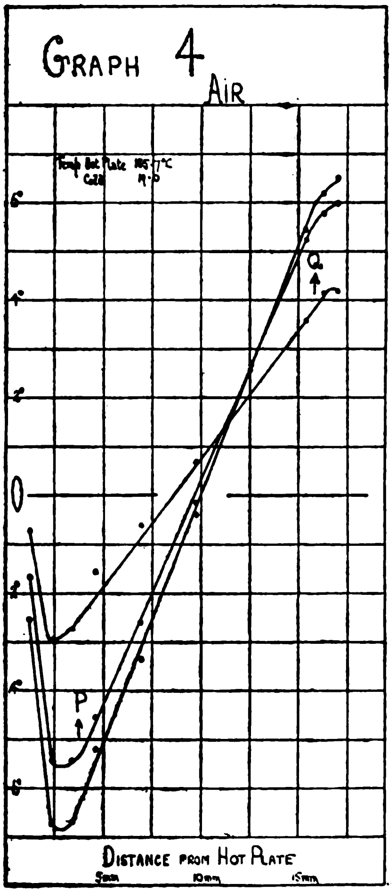


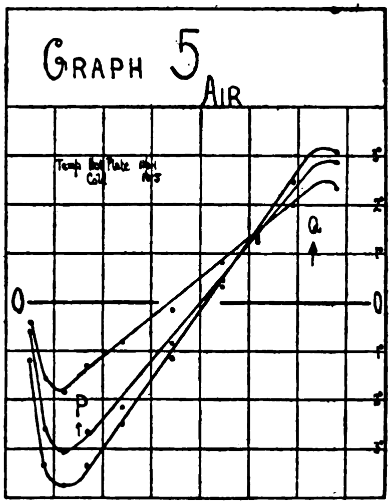


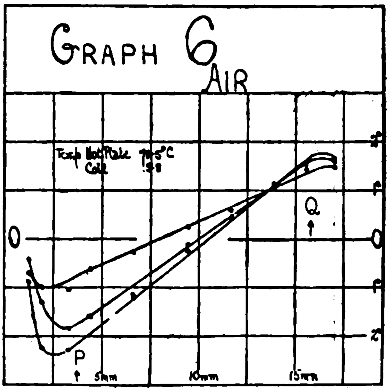


Graph 7 shows the method of extrapolating to zero diameter. The diameters of the couples are marked as abscissæ, the measured thicknesses of α, β, γ and δ being shown by the points W, X, Y and Z. Ordinates below these points in 0—0 denote the *total* differences in degrees between the very thin couple (α) and each of the couples β, γ and δ at the points P and Q. A series of curves was obtained passing through four points for each gradient, and by producing them through the point W the positions could be found where they meet the axis for zero thickness.

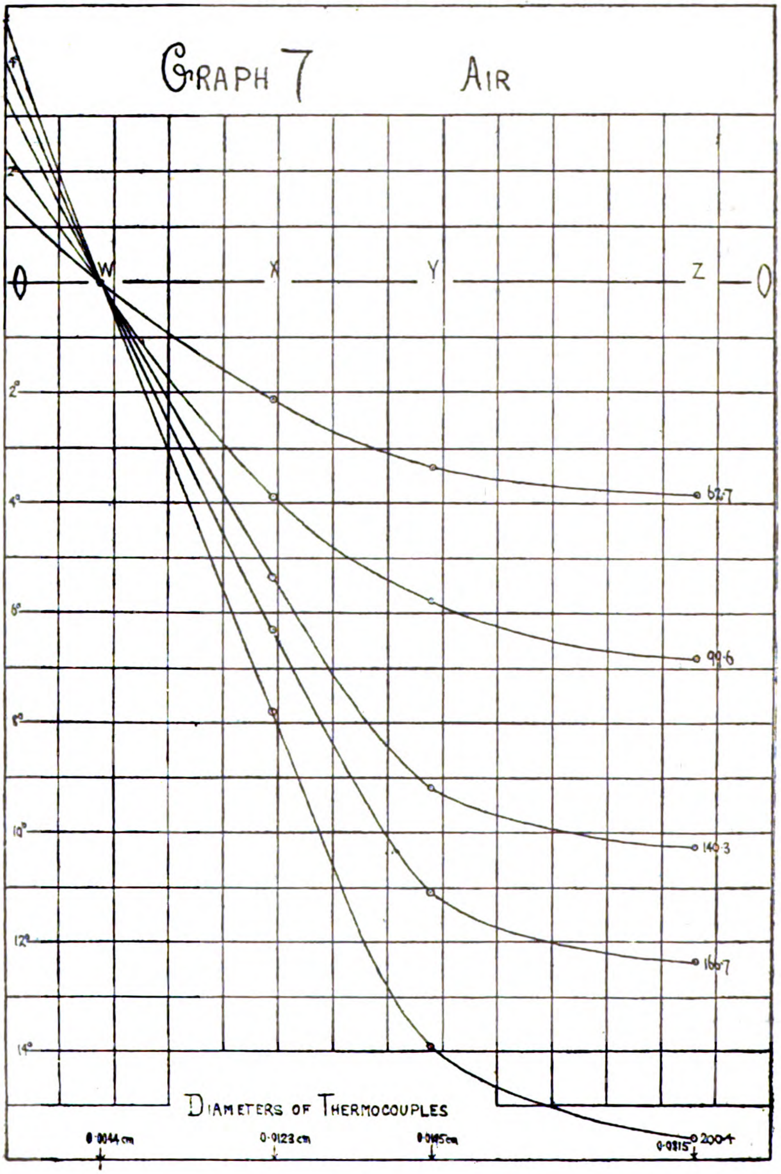
Graph 8 was obtained from Graph 7, the temperature differences between the hot and cold plates being shown as abscissæ, whilst the ordinates are the *total* variations in degrees between the infinitely thin and the several couples, between the points P and Q. It is seen from Graph 8, that, when the plates differ by 200°C., the *total* difference between the couple of zero diameter and the (α) couple between these points is 4·8°, for the (β) couple 12·5°, for the (γ) 18·7°, and for the (δ) 20·4°C. Also the four curves obtained show that these differences are almost linear functions of the temperature differences between the hot and cold plates. Further, it is to be noted that with the α, β and γ couples, that is, up to a diameter of about 0·020 cm., the difference varies fairly uniformly with the diameter, but afterwards increases very slowly with increase of thickness, for at 200°C. where the difference for the γ couple (diameter 0·0195 cm.) is 18·7°, for the δ couple (diameter 0·0315 cm.) it is only 20·4°C.





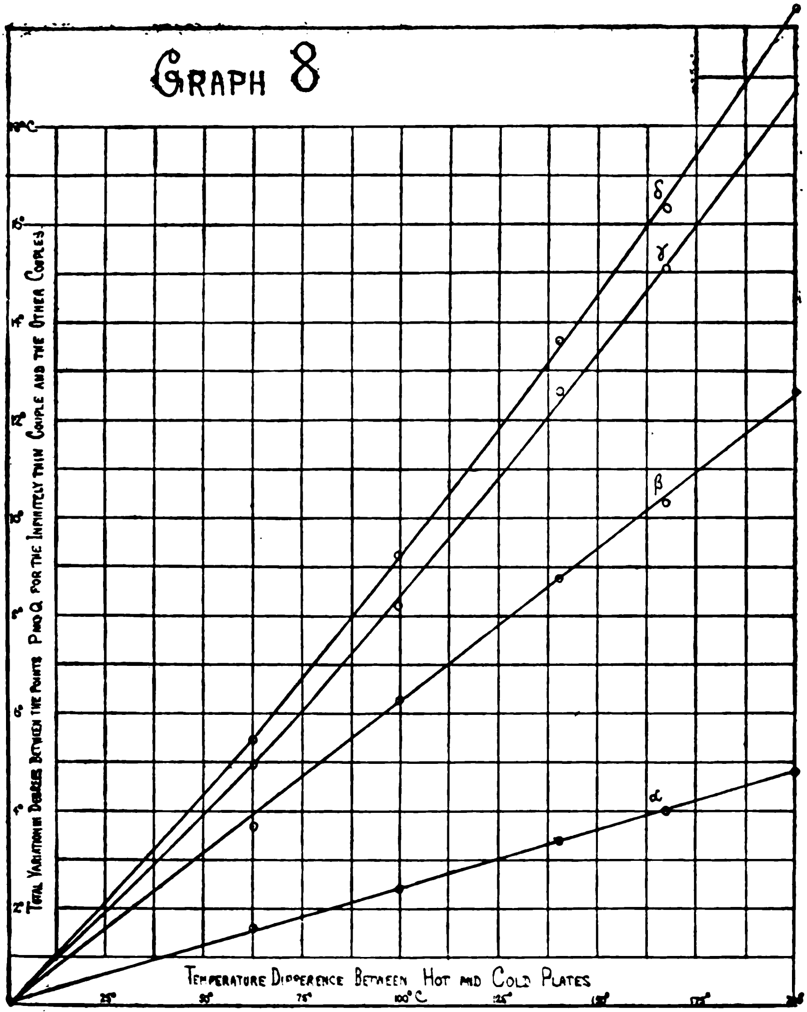


If it be assumed that the couple of zero thickness indicates the correct temperature, it is interesting at this point to refer again to Graph 1 to see the effect of applying the necessary correction. It has been pointed out already that the *total* correction to be applied to the very thin couple between the points P and Q would be 4·8°, but at *P* a correction of about 7° and at *Q* about 14°, that is, a total correction of 21°C., would be required in order to obtain the uniform temperature distribution as represented by the straight line. It follows, therefore, that with air at atmospheric



pressure, if the infinitely thin thermocouple records the true temperature there is a considerable temperature "fall" in front of the hot plate, and a "rise" in front of the cold plate. This was found to be the case with air and carbon dioxide for all temperature differences of the plates, and as will be shown later the gradient across the main portion of the gas for carbon dioxide was less than for air.

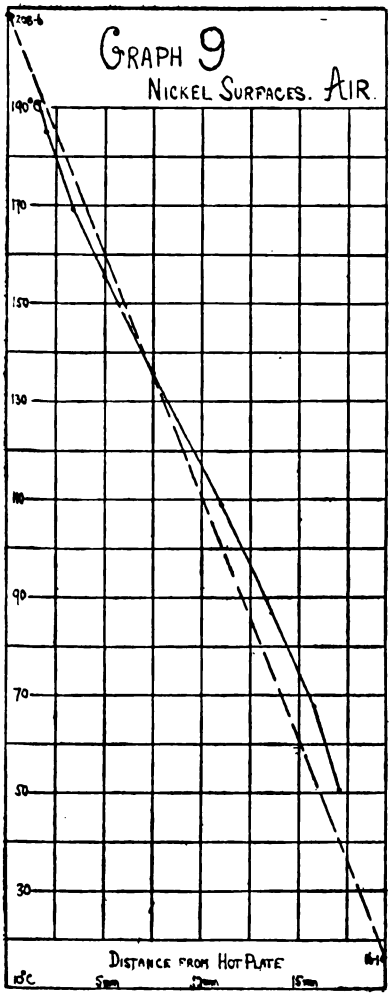
Bright Nickel Surfaces.—Experiments were next carried out with highly polished nickel surfaces on the horizontal plates. The couples were re-calibrated and in re-assembling the apparatus the very thin couple was broken. It was very fragile, due to its extreme thinness, and became considerably more so on prolonged heating.

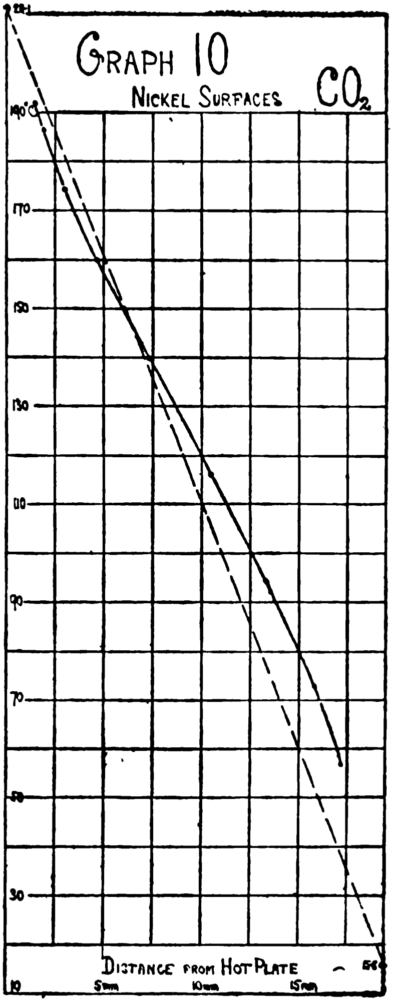


Another similar couple was fixed on the platform and calibrated, the order of the couples now being δ, β, α, γ. A new calibrated couple had also to be fixed on the hot plate.

Graphs 9 and 10 were obtained using the new (α) couple in air and carbon dioxide respectively, the temperatures of the plates being almost the same, viz., 208·6° and 16·1° and 211·1° and 15·8°C. in the two experiments. A comparison of the two shows one feature of importance in that the temperature slope in carbon dioxide is less than in air under similar conditions and that the temperature of the carbon dioxide is lower near the hot plate and higher nearer the cold plate than in the case of air. This point is also made very clear by Graph 11, giving two other sets of readings for the (*a*) couple in air and carbon dioxide for temperatures of 201·5° and 16·2° for air, and 201·2° and 16·6°C. for carbon dioxide.

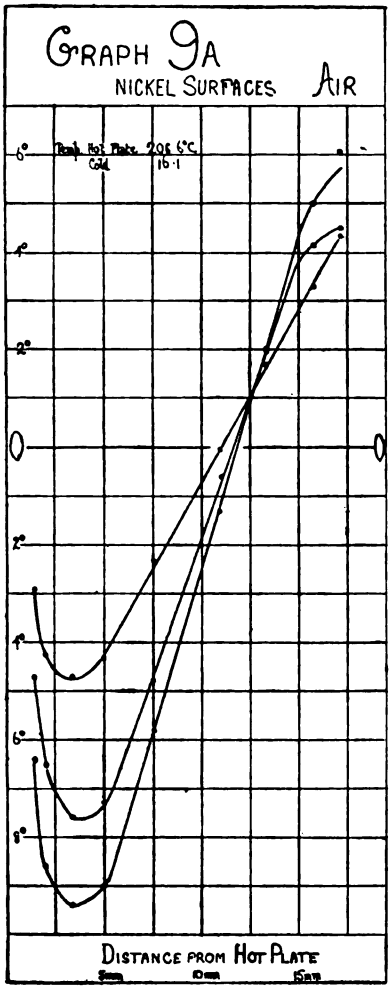
Graphs 9A and 10A are graphs of differences relating to the curves of Graphs 9 and 10. In all cases when comparing these two gases, it was found, as in these graphs, that the slopes of the line of temperature differences were slightly greater in carbon dioxide than in air. This would mean that if graphs similar to 7 and 8 were constructed for carbon dioxide the differences between the infinitely thin couple and the several couples would be slightly greater in carbon dioxide. On comparing Graphs 9 and 10 it is seen that at a distance of 4 mm. from the cold plate in air, the

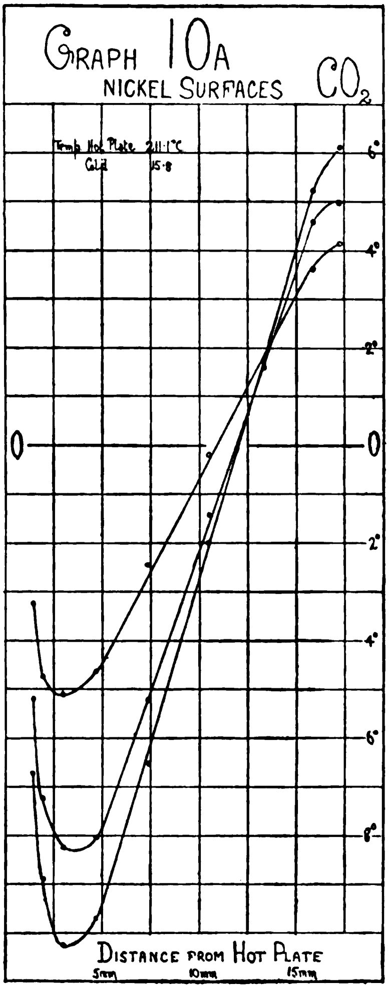




recorded temperature is 14°C. above the line of uniform temperature distribution, whilst in carbon dioxide it is 20°C. Thus if allowance were made for the infinitely thin couple the gradient would still be less steep in carbon dioxide than in air.

Lamp-Black Surfaces.—The horizontal plates were next covered with lamp-black and experiments carried out as before. It was thought that if these difference effects were due to radiation there should be a considerable change in the temperature distribution on comparing curves with the highly polished nickel surfaces and with the dull black surfaces.

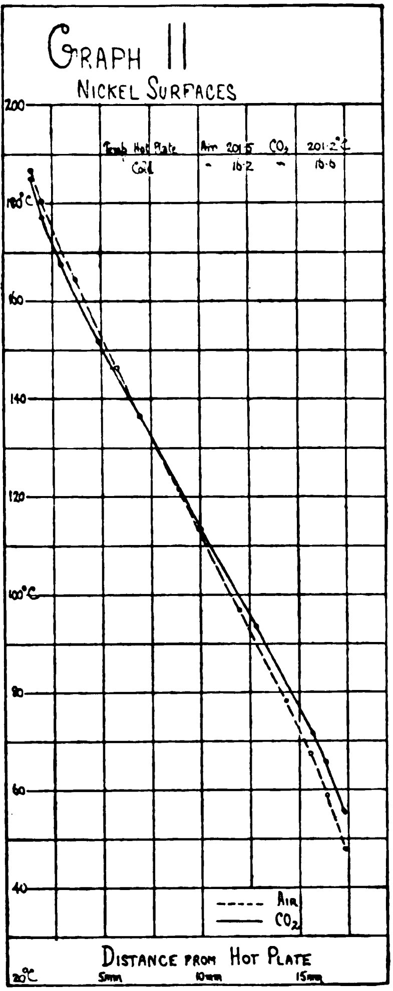




Graph 12 gives the results with air for bright nickel surfaces and Graph 13 with black surfaces, the plates being about the same temperatures in the two experiments. Graphs 12A and 13A show the corresponding differences. The curve of temperature distribution crosses the straight line of uniform gradient nearer the hot plate with the black surfaces, whilst in the colder portion of the chamber the temperature, at say *Q*, with the black surfaces is considerably higher than with the bright surfaces.

Using the black surfaces, Graphs 14 and 14A refer to experiments with hydrogen between temperatures of 206·4° and 23·5°C. and Graphs 15 and 15A to experiments with carbon dioxide between temperatures of 205·5° and 20·7°C. It is seen that the differences with carbon dioxide are about four times greater than with hydrogen.

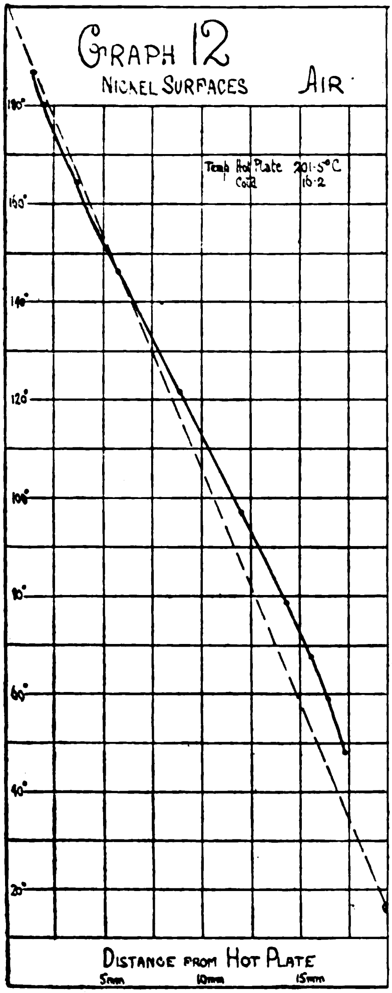
On comparing 13 and 15 where experiments are carried out in air and carbon dioxide with black surfaces, it will be seen that the temperature distribution curve in carbon dioxide as measured with the (*a*) couple is less steep than in air as was seen to be the case with nickel surfaces (Graphs 9 and 10), whilst a comparison of 13A and 15A shows that for the black surfaces the slope of differences is slightly greater in carbon dioxide than in air as was pointed out for nickel surfaces (Graphs 9A and 10A).

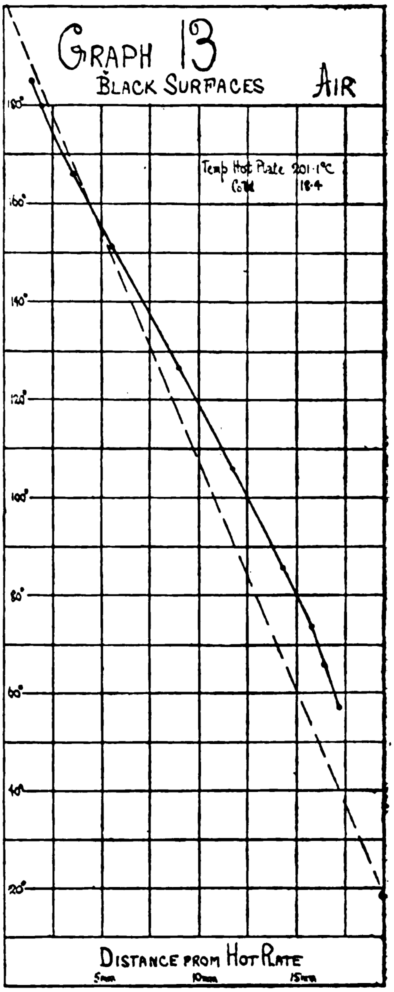


DISCUSSION OF RESULTS.

It remains to consider the process by means of which the couples take up their temperatures and to find some explanation of the influence of the diameter of the wires. The factors that must be taken into account are probably limited to:—

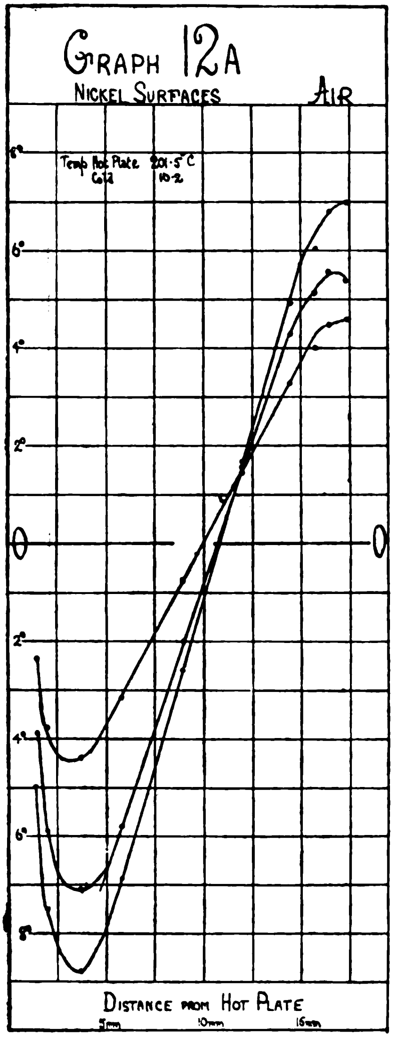
(1) The interchange of energy between the gas molecules and the couples,
(2) the radiation received and emitted by the couples,
(3) the residual gas layers condensed on the couples,
(4) the conduction of heat along the wires from the actual junctions.

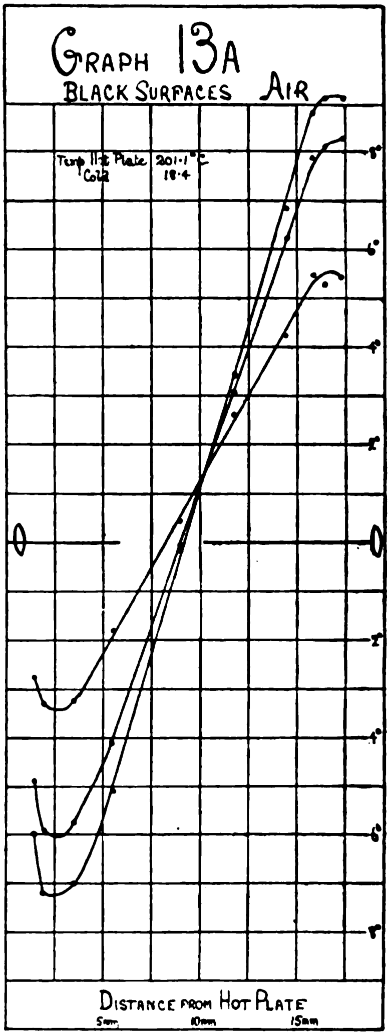




With regard to No. (4) it has been already shown that precautions were taken in designing the horizontal platform so as to eliminate this effect as far as possible by having considerable lengths of the wires in an isothermal layer, and it is probable that any effect due to conduction is practically negligible.

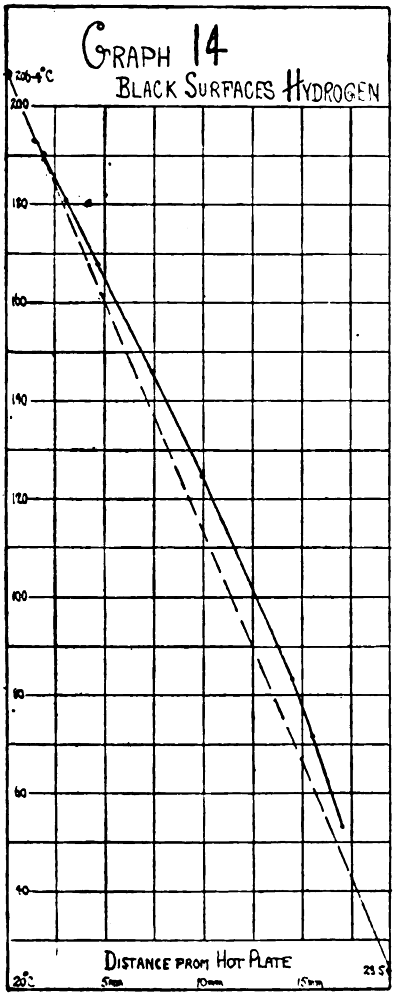
The subject of adsorbed gas layers is one of extreme difficulty, and there is considerable difference of opinion regarding two rival theories, one, that the layer may be several molecules thick, and the other, that it is monomolecular. Experiments have been carried out for instance, showing that charcoal can adsorb many times its own volume of gases at ordinary temperatures and pressures. Other workers have shown that gases like carbon dioxide and ammonia form a film several molecules thick when brought in contact with glass fibres that have been previously heated to a high temperature at low pressures. Considerable volumes of gases can be detached from the glass walls of a vessel when heated at very low pressures, and estimations have been made that the layer may be as many as 20 molecules thick. Other experiments have been devised in support of this theory showing that the

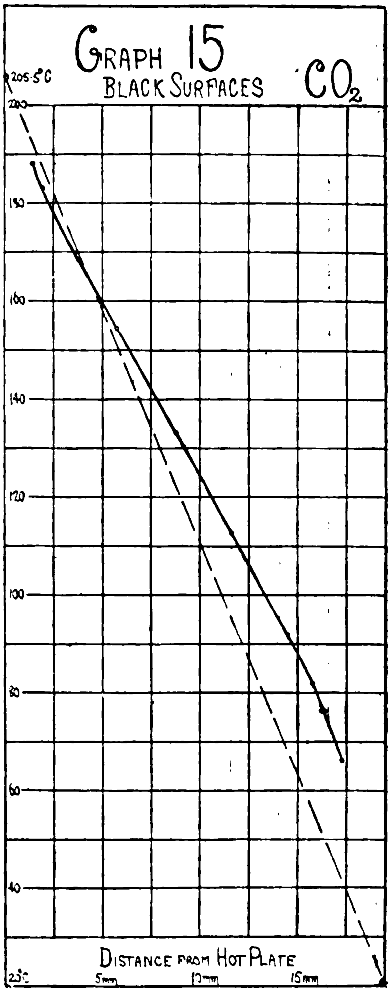




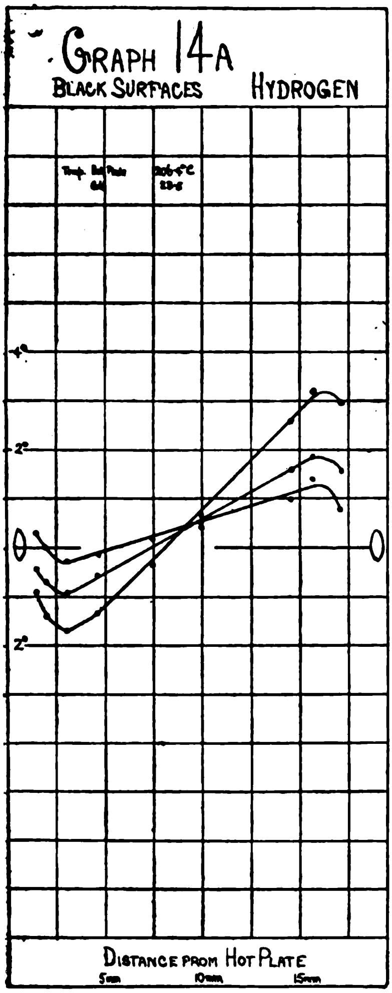
range of molecular forces may extend to a distance equal to a considerable number of molecular diameters.

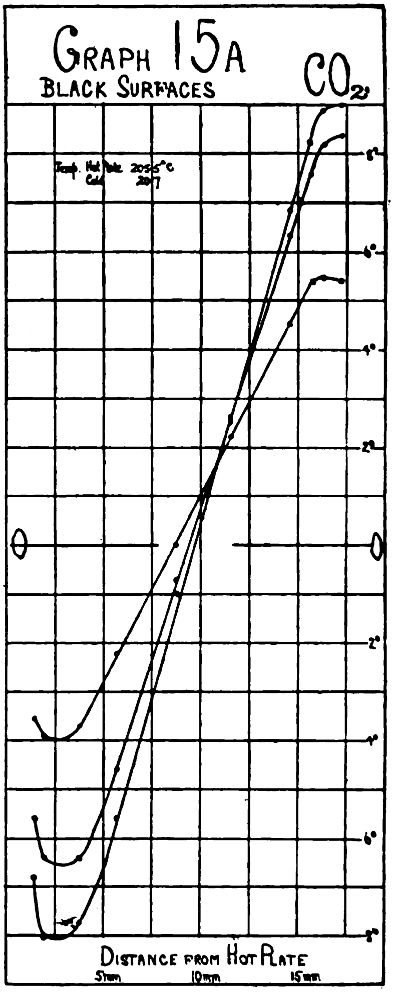
On the other hand, a large amount of work has been carried out by many workers and especially Langmuir, which gives very strong support to the theory of an adsorbed layer one molecule thick. They also point out that the large amount of gas adsorbed by charcoal depends upon a capillary condensation theory, due to the known fact that the vapour pressure of a liquid inside a fine capillary, the walls of which are wet by the liquid, decreases greatly with the decrease in diameter of the capillary. With regard to the adsorbed film on glass fibres, they point out that if the gases be very carefully dried, the adsorbed film is only monomolecular and suggest that all the gases used like ammonia and carbon dioxide, being very soluble, are merely dissolved in a film of water on the glass. It must be admitted that most of the evidence seems to be in favour of the single layer. If, however, there be





comparatively thick layers it seems probable that the thickness of the layer would depend upon the diameter of the wires, and it would then be possible to suggest an explanation of the results by giving special physical properties to the layer—a variation in thermal conductivity for instance—different from those of the gas. The thickness of the layer required, however, would be considerably greater than several molecules, so that it would seem to be futile to suggest any explanation based on such a supposition which is not supported by experimental evidence.





With regard to No. (2), radiation seems to play an important part in the experiments described in this Paper. Perhaps the best evidence is obtained from a comparison of Graphs 12 and 13, where experiments are carried out with the *same* gas, air, but with surfaces of highly-polished nickel and of lamp-black respectively. It follows that the quantities of radiation from the two surfaces in the two cases must be quite different. It is seen that in the experiment with the black surfaces the recorded temperature distribution curve crosses the straight line of uniform temperature distribution nearer the hot plate than in the case of the experiment with the nickel surfaces, whilst nearer the cold plate, as has been already pointed out, the temperature distribution curve is about 6°C. higher with the black surfaces than with the nickel surfaces.

The amounts of radiation received and emitted by a couple for different positions in the chamber cannot be determined accurately. Stefan's formula is not applicable, especially with the polished nickel or brass surfaces. Still, it is instructive to make a *rough* calculation of these amounts of radiation by supposing that the fourth power law can be used. Consider the case with the lamp-black surfaces, the couples also having practically similar surfaces. Let Fig. 2 represent a central section of the experimental chamber. Suppose as in some of the experiments described in this Paper the absolute temperature of the hot plate is 470, and for convenience of calculation let the temperature of the cold plate be 270. Divide the distance between the two plates into five equal parts, and let them be represented by the four points *A*, *B*, *C*, *D*. Then, if the points be on the straight line of uniform temperature distribution, their absolute temperatures would be 430, 390, 350 and 310 respectively. Then, applying Stefan's Law, it can be shown that the ratio of the amount received to the amount emitted in the four cases is 1 : 1·26, 1 : 0·85, 1 : 0·55 and 1 : 0·37. Even allowing that the assumptions made in the calculation may result in a considerable error, it is seen that near the hot plate a couple receives less radiation than it emits, while at the points *B*, *C*, *D* it receives a gradually increasing excess of radiation on approaching the cold plate.

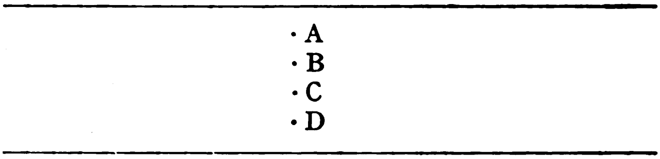


FIG. 2.

On referring to all the graphs of differences we see a maximum effect a few millimetres from the hot plate. On proceeding towards the cold plate, a point is reached where the lines intersect, suggesting that here the amounts of radiation received and emitted are the same, whilst still nearer the cold plate an excess of radiation is received, and the recorded differences of temperature gradually increase towards the plate The same applies to Graphs 1, 9, 10, 12, 13, 15, all of which show a " dip " near the hot plate, and the gradual slope upwards above the straight line on going towards the cold plate.

With the same assumptions as before, a rough calculation can be made of the distance from the hot plate where the amounts received and emitted by a couple are the same. Taking the figures of the last calculation, the point would be at a distance of rather more than one-fourth of the distance between the plates from the hot plate, and Graph 13 shows that the curve of temperature distribution crosses the straight line at about this distance. The best test, however, is to calculate the position of this point for different temperature gradients between the plates, and it is found that the point approaches the cold plate very slowly at first with decrease of temperature gradient, but much more rapidly when the gradients are small.

An examination of a large number of temperature distribution curves for different gradients fully confirmed this view.

Thus it is evident that radiation plays an important part in determining the temperatures recorded by the couples, but that it is not the *sole* cause of the temperature differences is shown by employing *different* gases in carrying out experiments under exactly identical conditions. Graphs 14 and 15, where the gases hydrogen and carbon dioxide respectively are used, show entirely different results, although the amounts of radiation must be the same in the two cases. The graphs of differences (14A and 15A) for the same experiments show that the temperature differences are about four times as great in carbon dioxide as in hydrogen. It is evident, therefore, that the nature of the gas is of considerable importance, and it is advisable at this point to consider briefly some of the theories relating to molecular impact and the interchange of energy between gas molecules and a solid with which they collide. Nearly all these theories have been suggested to account for the fact that certain experiments on the conduction of heat indicate that there is a poor interchange of energy when molecules collide with walls which are at a higher or lower temperature. One theory claims that molecules of all kinds show little or no tendency to be regularly reflected from a solid surface ; that, instead, they condense and re-evaporate in a direction independent of the direction of incidence. On decreasing the temperature, the mean kinetic energy of the molecules becomes less and they evaporate less readily owing to the restraint imposed upon them by the force of molecular attraction. So long, however, as the rate of evaporation is greater than the rate of condensation the molecules of the first layer do not remain long enough to become covered by the others.

Another theory partly supports this view, but claims that a fraction of the molecules condense and re-evaporate, but the remainder are regularly reflected. One theory which has been suggested takes into account the attractive and repulsive forces existing between the molecules of the solid and the gas. A gas molecule approaching a hot plate may strike a plate molecule and be sent back into the gas with an energy greater than its previous energy, but less than the energy equivalent to the temperature of the plate, whilst other molecules, colliding several times with the surface before being able to escape, take up a larger store of energy, part of which is lost, however, when the molecules do work in escaping against attractive forces existing at the surface of the plate.

Experiments illustrating this imperfect interchange of energy have been carried out by Knudsen,* and by an entirely different method by Soddy and Berry.† The latter, in an experiment on thermal conductivity with gases at low pressures, found the loss in watts from a heated platinum strip of known area, which was at a temperature of about 40°C. higher than a cylindrical enclosure kept at constant temperature. From the dimensions of the apparatus, the experimental value of the thermal conductivity could be determined. The theoretical value could also be found knowing the number of impacts and the amount of heat required to raise one molecule through 1°C., and assuming perfect interchange of energy on impact. The ratio of the two gives a coefficient analogous to Smoluchowski's "Coefficient of Thermal Accommodation." Using bright platinum surfaces, Soddy and Berry found that its values for hydrogen were 0·15 at 100°C. and 0·25 at −185°C. ; for helium the values were about twice as great, while larger values were found for carbon dioxide and nitrogen. It appears to be fairly well established, therefore that the transference of heat from a solid by molecular impact takes place comparatively slowly, and varies with the gas.

---

* Ann. der Phy., 34, 593 (1911).

† Proc. Roy. Soc., November (1910).

There can be no doubt from the evidence produced so far that the temperature differences are due to two main factors—radiation, and the nature of the gas. An explanation has already been given explaining the effects of radiation in different parts of the chamber, but it is now necessary to suggest why the four couples in the same horizontal plane record different temperatures, and, furthermore, why the thickest couple is lowest near the hot plate and highest near the cold plate.

Consider a couple at the point A in Fig. 2, where it radiates more energy than it receives as radiation. It would, therefore, be lower in temperature than if radiation were negligible. The gas molecules, however, near the point A would not be lowered perceptibly in temperature, since gases are practically transparent to radiation. Therefore the couple would be at a temperature lower than the surrounding gas, so that energy would be transferred by impact in an endeavour to equalise the temperatures.

Consider now the relative *effects* of the two factors. The nett loss of energy by radiation for each couple would differ in amount proportional to its radiating surface. Let the amount be represented by Kr, where r is the radius. They would gain energy by molecular impact, again proportional to their surfaces and equal to $K'r$, K' being a constant for the given plane considered, since the condensation and evaporation takes place at the same rate for the same temperature, but would vary in different planes. There would, therefore, be a nett loss of energy for each couple proportional to $(K-K')r$—that is, the thicker the couple at the point considered the lower would be its temperature. In the same way at, say, the point D, near the cold plate, the couples receive an excess of radiation $(K''r)$, and would be higher in temperature than the surrounding gas. They would therefore lose energy by molecular impact $(K'''r)$. The gain still being $(K''-K''')r$ for each couple, the thickest couple would now give the highest temperature, a result which agrees with experiment.

Further support is given to this view by Graph 8, which shows that for the three thinnest couples their differences in temperature from the infinitely thin couple vary almost as the radii of the wires.

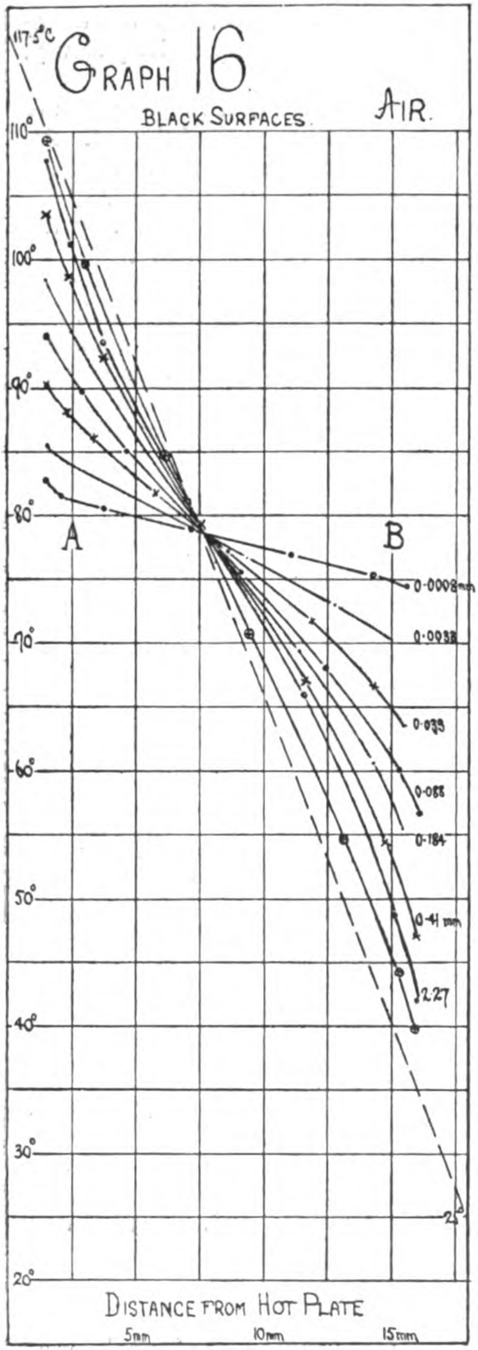
Since experimental evidence has shown that different gases have different "Accommodation Coefficients," we may look to this fact for an explanation of the difference in the results obtained with different gases.

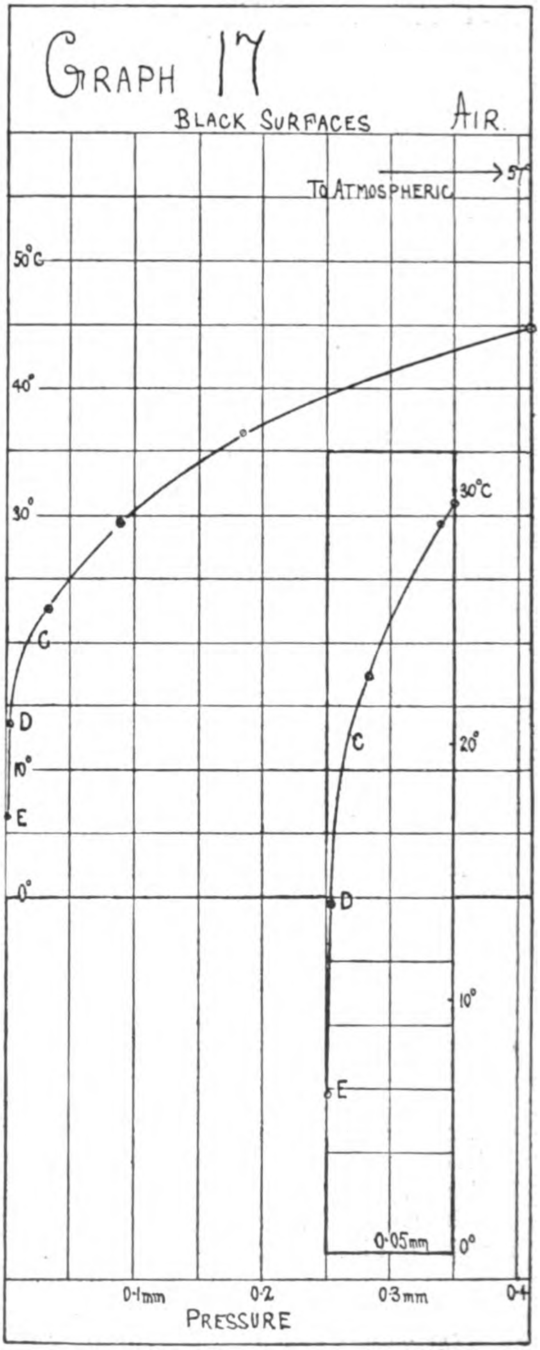
The experimental results and deductions of this Paper seem to have a wide application to measurements of temperature in industry. They suggest that in the measurement of temperature, thermocouples, mercury-in-glass thermometers, and resistance thermometers cannot be relied upon as instruments of precision unless they are used under conditions which are identical with the black-body enclosure.

In conclusion, the author wishes to express his thanks to Prof. Gwilym Owen for his kind interest and encouragement.

NOTE ADDED OCTOBER 31, 1925.

On continuing the experiments in air at low pressures a new set of couples was used, but results are given for the new *a* couple only. Graph 16 shows the results


117.5°C
GRAPH 16
BLACK SURFACES
AIR
110°
100°
90°
80°
70°
60°
50°
40°
30°
20°
A
B
0·0008mm
0·0038
0·033
0·088
0·184
0·41 mm
2·27
24
DISTANCE FROM HOT PLATE
5mm
10mm
15mm


GRAPH 17
BLACK SURFACES
AIR
TO ATMOSPHERIC
57°
50°C
40°
30°
10°
0°
C
D
E
30°C
20°
10°
0°
C
D
E
0·05mm
0·1mm
0·2
0·3mm
0·4
PRESSURE

obtained at various pressures, the temperatures of the hot and cold plates being kept constant. These results give strong confirmatory evidence for the correctness of the explanation given for gases at atmospheric pressure. All the graphs pass through a point where the amounts of radiation received and emitted by the couple are equal. It has been shown that between this point and the hot plate there is a nett loss of energy due to radiation alone, whilst between the point and the cold plate there is a nett gain.

It follows immediately that the lower the pressure the less will be the energy transferred by molecular impact, so that in front of the hot plate the couple falls in temperature until a state of equilibrium is reached which will depend upon the pressure. It follows also that these two surface effects will depend upon the thickness of the couple, so that by using a single couple we immediately deduce that thicker couples must read lower temperatures near the hot plate and higher temperatures near the cold plate, and that these readings would vary with the nature of the gas.

An interesting point regarding the energy transferred by molecular impact is shown on taking two fixed points *A* and *B* in the gas, and finding the temperature difference between them at different pressures.

At atmospheric pressure this is 57·0°C., and for the several pressures 50·6, 44·8, 36·6, 29·5, 22·7, 13·7, and 6·3°. These temperature differences are plotted against the pressures in Graph 17.

It is seen that the temperature difference between the points falls slowly and fairly uniformly from atmospheric pressure to a pressure represented by the point *C*, where the mean free path is about 0·3 mm. At lower pressures the rate of fall is much greater, and at the point *D* the mean free path is approximately equal to the distance between the plates when the curve becomes considerably steeper.

This can be explained as follows: When energy is transferred by molecular impact the colliding molecule immediately receives energy from the gas molecules in the vicinity—that is, the conductivity of the gas comes into play. On reducing the pressure until the mean free path of the molecules is of the same order as the dimensions of the chamber, conduction ceases, and we have then simply a molecular flow between the plates, the molecules receiving energy directly from the walls, and this state would be represented by the steep portion of the curve at the point *D*. On still further reducing the pressure, the fall in temperature would vary directly as the number of molecules, so that we would expect the portion of the curve *DE* to be a straight line, as indicated in the graph.

DISCUSSION.

Mr. R. S. WHIPPLE said that as the readings of the thermocouples were so much affected by the nature of the gas in which they lay and so little by the change of surface from black to bright he could not help feeling that the author had under-rated the effect of gaseous conduction as compared with radiation. Would it not be well to construct the thermocouple leads of horizontal stretched wires so that they might be made to coincide with isothermal layers of gas?

Mr. C. R. DARLING congratulated the author on the very large number of observations he had taken, but said that in spite of this he felt that the conclusions which had been reached needed confirmation: convection must surely play a considerable part in such phenomena. The Paper constituted a warning, however, against the incautious use of thermocouples. The method of interpolating to zero attributed to Kreisinger and Barkley was, he believed, first put forward by Smithells in connexion with his work on gas films.

Dr. J. S. G. THOMAS said that the large amount of patient work described in the Paper is of great interest to industries in which thermocouples are much employed. If he could fully accept the author's low estimate of the reliability of thermocouples he should feel considerable uneasiness, but he was inclined to think that the effect of convection had been under-estimated: convection currents are excessively difficult to eliminate, as was found in such work as that of Boys on the gravitation constant, and in industrial measurements large allowances have to be made for them. The author's results suggest that in some cases there may be errors amounting to 50 per cent. of the actual temperature, but there is no reason to believe that in industry such errors as that occur, in view of the precautions taken. An excellent study of the effects of conduction has been given by Daynes in the account of his katharometer, and he believed this might throw light on the results obtained by the author. As regards the method of interpolation mentioned by Mr. Darling, he rather thought that Nichols and Hull were before Smithells in that matter.

Dr. GEOFFREY MARTIN said that though not himself a physicist he had to use thermocouples in attempting to balance the input and output of heat in a cement-making process, and he would be very glad of advice as to the cause of gross errors which he had encountered.

Mr. GUILD pointed out that the readings of the thermocouples depended on the properties of two metals. The problem might be simplified by using a single metal in the form of a resistance thermometer.

Mr. J. H. BRINKWORTH said that even if a platinum resistance thermometer were used, the readings would depend on the nature of the gas. He felt a personal interest in the subject of the Paper because it had a bearing on some measurements of the ratio of the specific heats of hydrogen made by Mr. Partington and by himself, the former's values being higher than his own. In these experiments the temperature was measured with a platinum resistance thermometer and a correction had to be made for the conductive effect of the gas on the platinum, this effect having been standardized by measurements made in air. In fact, however, the correction applicable in hydrogen would be smaller than that applicable in air, and taking the author's figures it appeared that Mr. Partington's results should accordingly be reduced by approximately the amount which would make them agree with his own.

Mr. R. S. TROOP (communicated): The author of this Paper is to be congratulated on some very useful, interesting and well-planned experiments dealing with a subject whose application in industry is rapidly growing. There are many occurrences in industry of "unequally heated enclosures" where accurate temperature measurements are required, and the Paper indicates some precautions necessary to attain this accuracy when thermocouples are used, and the difficulty of obtaining "instruments of precision" under these conditions. The results also show that due care must be taken in making deductions from thermocouple readings and allowances made for the effects recorded in the Paper before too great stress is laid on small peculiarities in temperature readings. The work on the effect of atmosphere on temperature readings will have particular interest for those dealing with kilns, ovens, flues, etc. It is good to note that Mr. Mandell promises us further work on the subject. The question of the effect of the materials of the thermocouple is not dealt with in the Paper, and I should like to ask whether this has been considered by the author. At higher temperatures this may be important, in view of Sir G. Beilby's work on the effect of atmosphere on the recrystallisation of metals, their surface adsorption, etc. One would like to know also how atmospheric differences would affect the e.m.f.s of platinum-platinum-rhodium and of nickel-chrome couples which are of considerable industrial importance.

AUTHOR'S reply (communicated): With regard to the references in the discussion that the effects of convection may be considerable, it is necessary to point out that we have, in effect, a layer of gas about 2 cm. thick bounded by a large, hot upper plate and a lower cold one some 12 cm. in diameter, so that there would presumably be little tendency for the circulation of convection currents in the gas. It is difficult to see how a more ideal arrangement could be designed.

The remarks of Mr. Guild and Mr. Troop contain suggestions which would undoubtedly be of value in the event of further work being done on the subject.

Three references are made in the discussion to the effect of the conductivity of the gas. A note added to the present Paper is in effect a reply to that criticism, as it shows the intimate relations between the transference of energy to the couples by molecular impact, and the conductivity of the gas.

VII.—PHOTO-ELECTRIC RADIATION PYROMETER.

By Prof. F. A. LINDEMANN, F.R.S., and T. C. KEELEY.

Read at Oxford, July 4, 1925.

ABSTRACT.

By means of two photo-electric cells with suitable coloured filters the energy radiated in two distinct spectral bands is compared. By combining the ascertained sensitivities of the two cells and their filters with the radiation law the black-body temperature of the radiator can be determined.

SOME years ago one of the authors suggested that by measuring the photo-electric currents produced by the same source of light on two metals sensitive to different parts of the spectrum it should be possible to obtain an estimate of the temperature of the source of light.* Although the original suggestion was directed particularly to the determination of stellar temperatures, the method is obviously suitable for terrestrial sources. It may be of interest to give a preliminary account of the instrument designed for this purpose, more especially since a pyrometer based on the same principle made in the General Electric Company's laboratories has recently been described.†

The construction is shown in Fig. 1. By means of the lens *A* the light from the source is focused on the fixed diaphragm *D*, so that the light enters the apparatus always in the same direction. The lens *B* renders the light parallel, and it is then partly transmitted, partly reflected, by the half platinised mirror *M*. The two beams are focused by the lenses *C* and *D* on to the optical wedges W_R and W_K, and after passing through two coloured filters F_R and F_K, they enter the photo-electric cells *R* and *K*, which contain rubidium and potassium respectively. The cells are connected in opposition to the needle of the electrometer, so that when the current is the same in each the electrometer shows no deflection. The electrometer needle is connected to earth through a high resistance leak (of the order of 10^{10} ohms).

A source of known temperature is used to fix the scale. The wedge W_K is set at some convenient reading, say d_0, and the coarser wedge W_R is adjusted until the electrometer shows no deflection. Final adjustment is rendered more accurate by means of the shutter *S*, which is opened and closed by hand; the electrometer should show no flicker as the cells pass from the illuminated to the dark condition. This adjustment made, the wedge W_R is fixed permanently in position.

When the instrument is focused on the source whose temperature it is desired to measure, the wedge W_K is moved until the electrometer shows no deflection—i.e., until the current from the two cells is equal. Suppose its reading is d_1, and that the source is at a higher temperature than the standard, so that d_1 is greater than d_0. Then the ratio in which the light entering the potassium cell must be reduced so that its current balances that from the rubidium cell, is $k \log (d_1 - d_0)$, where k is the "wedge constant." As will be seen, this is a measure of the temperature of the source.

---

* Monthly Notices, R.A.S., March (1919).

† Journ. Sci. Inst., Vol. II, No. 6, p. 177, March (1925).

Suppose the currents produced by unit light energy on the potassium and rubidium cell respectively are given by $f_K(\lambda) . \delta\lambda$ and $f_R(\lambda) . \delta\lambda$, and that the ratio transmitted by the two filters are $\varphi_K(\lambda) . \delta\lambda$ and $\varphi_R(\lambda) . \delta\lambda$. Then, for a black body source at a temperature T_0 the currents produced by the two cells will be respectively given by

$$i_K = c_1 \int f_K(\lambda)\, \varphi_K(\lambda) \,.\, e^{-\frac{a}{\lambda T_0}} / \lambda^5 \,.\, d\lambda$$

$$i_R = c_2 \int f_R(\lambda)\, \varphi_R(\lambda) \,.\, e^{-\frac{a}{\lambda T_0}} / \lambda^5 \,.\, d\lambda$$

where c_1 and c_2 are constants depending on the apparatus.

Integration extends over the wavelength range to which the combined cell and filter system is sensitive, Wien's radiation law being used, since for the wavelengths in question, this differs from Planck's by not more than $\frac{1}{4}$ per cent. even at 5,000. As the cell and corresponding filter are always used together, we can write $f(\lambda) . \varphi(\lambda)$ as $F(\lambda)$, and we have

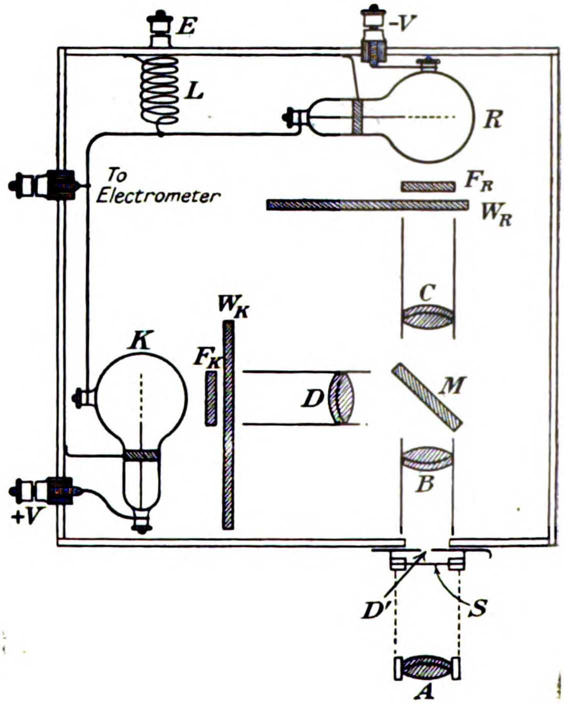


FIG. 1.

$$\left.\begin{aligned} i_K &= c_1 \int F_K(\lambda) e^{-\frac{a}{\lambda T_0}} / \lambda^5 \,.\, d\lambda \\ i_R &= c_2 \int F_R(\lambda) e^{-\frac{a}{\lambda T_0}} / \lambda^5 \,.\, d\lambda \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Suppose now that the pyrometer is focussed on a source of temperature T_1. The currents produced will be

$$\left.\begin{aligned} i'_K &= c_1 \int F_K(\lambda) e^{-\frac{a}{\lambda T_1}}/\lambda^5 \,.\, d\lambda \\ i'_R &= c_2 \int F_R(\lambda) e^{-\frac{a}{\lambda T_1}}/\lambda^5 \,.\, d\lambda \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

If the currents in (1) are made to balance by adjustment of the wedge W_R, then the currents in (2) will not balance. The distance the wedge W_K must be moved to bring about a balance will be given by

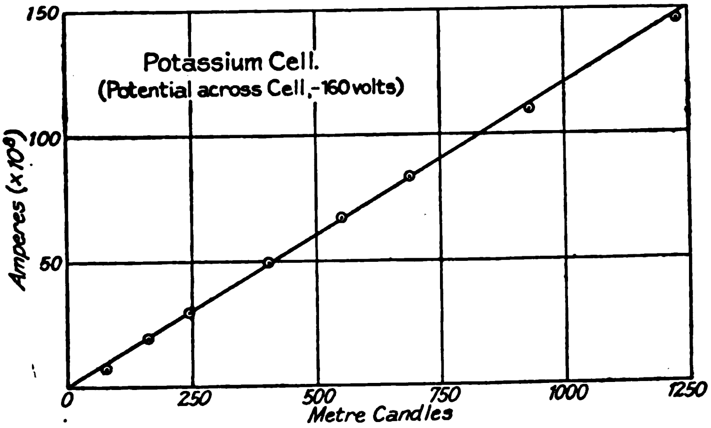


FIG. 2.

$$k \log (d_1 - d_0) = (i'_K/i'_R)/(i_K/i_R)$$

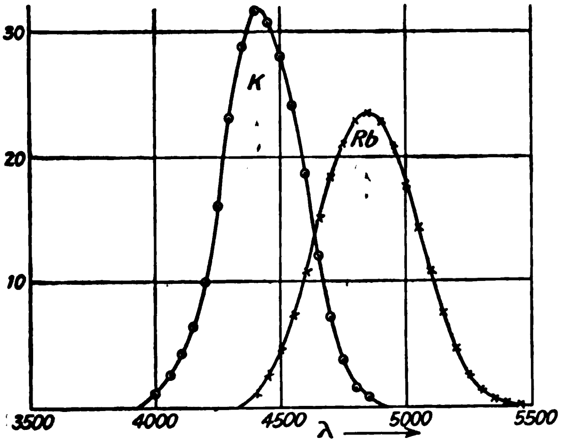


FIG. 3.

We have assumed in deducing the above result that the photo-electric current is proportional to the intensity of the light falling on the cell. This was verified for the type of cell used, as is shown in Fig. 2.

The form of the functions $F_K(\lambda)$ and $F_R(\lambda)$ may be found by illuminating the aperture of the pyrometer with monochromatic light from a constant deviation spectrometer, and measuring the currents from each cell separately. The source of light was a carbon filament lamp, the temperature of the filament being measured by means of an optical pyrometer. The two curves giving the sensitivities per unit energy received are shown in Fig. 3.

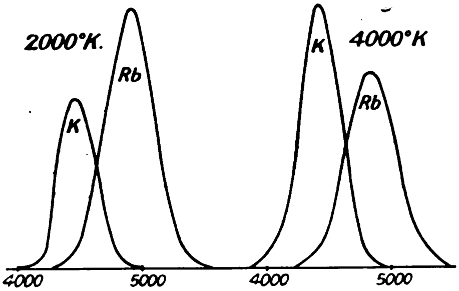


FIG. 4.

The filters used were chosen so as to accentuate the sharpness of the maxima due to the selective photo-electric effect. By combining these curves with the radiation curves at various temperatures from 1,800°K to 5,000°K, measuring the areas and finding their ratios, the readings of wedge W_K are calculated in terms of the temperature. Fig. 4 shows the respective values of the currents produced in the two cells at 2,000° and 4,000°, the scale of the diagrams being, of course, very different.

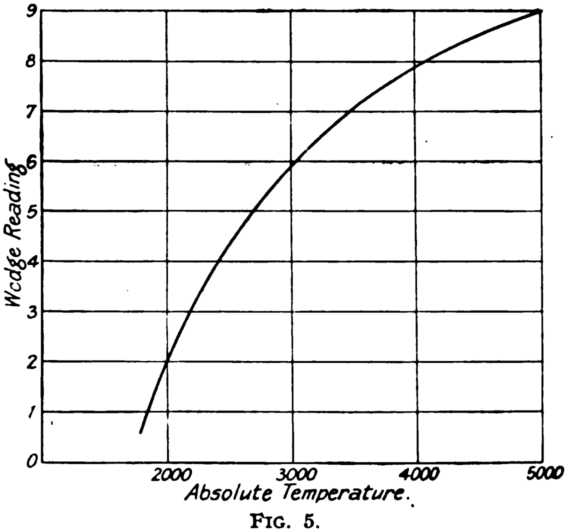


FIG. 5.

Fig. 5, giving the calculated curve, shows the temperature corresponding to any given reading of the wedge used. The wedge constant was found photoelectrically, and agreed with that given by Messrs. Ilford to less than 1 per cent., and was constant over the whole wedge, the result, of course, confirming the proportionality of light and photoelectric effect.

It will be seen from the last curve that at 2,000° a change of wedge reading of 1 cm. corresponds to about 160° ; at 3,000°, to 300° ; at 4,000°, to 700°. By reading to 1/10 mm. (and this setting can be repeated without any difficulty), the temperature at 2,000°, 3,000° and 4,000° can be found to an accuracy of 1·6°, 3° and 7° respectively. By the use of a finer wedge, temperatures over a more confined range could be measured even more accurately.

DISCUSSION.

Dr. C. CHREE : There seems a promising field for an instrument capable of even moderate accuracy at the high temperatures mentioned. The accuracy would presumably depend on the precision with which it measured known temperatures below 2,000°C., such as the melting point of platinum. It is a subject on which we look for enlightenment to the National Physical Laboratory.

Mr. F. E. SMITH : The author has shown the need for someone—preferably the Heat Department of the National Physical Laboratory—to discover a simple means of accurately reproducing a high temperature, such as the melting point of platinum, for standardisation purposes.

Mr. J. GUILD : I am particularly interested in the measurement of high temperatures. The photo-electric method is one of great promise in view of the high sensitivity. There are, however, a number of difficulties involved in the use of a method depending on the relative indications of two separate cells. Some of these were referred to in a Paper by N. R. Campbell and H. W. B. Gardiner, published in the Journal of Scentific Instruments for March, 1925, which contains an account of preliminary work on similar lines. I should be interested to hear if Prof. Lindemann has experienced any trouble due to inconstancy of the cells, variations in the " dark current," etc. My own feeling about photo-electric cells is that these are not yet instruments of such constancy of behaviour that we can safely determine characteristic curves, and regard these subsequently as instrumental constants in work of high precision. I should on this account prefer a null method in which one cell only is used. If filters be introduced to give the difference in wavelength sensitivity, there seems little point left in employing two cells. It is important to remember that measurements of this general type determine what is known as " colour temperature," as distinct from " brightness temperature," which is measured by optical pyrometers on a photometric basis. These temperatures differ from one another and from true temperature on the work scale, except in the case of radiators, which give full " black body " radiation. In the general case the scales are not directly comparable with one another without a complete knowledge of the emissive properties of the surface of the radiating material.

Dr. G. W. C. KAYE (communicated) : The several advantages, and not the least the relative simplicity of the photo-electric type of radiation pyrometer, which Prof. Lindemann describes, should lead to its extended use, at any rate for research purposes. The instrument will be a welcome addition to the other types of pyrometers in existence for exploring the region of really high temperatures. Prof. Lindemann's desire for a " jumping-off " temperature standard at about 2,000°C., which can be easily reproduced, is one that the N.P.L. will naturally bear in mind.

AUTHORS' reply (communicated) : We have always found our cells reliable and constant, and no difficulty has been experienced either with dark current or with a variation of sensitivity provided a luminous discharge is avoided. Of course, if we adjust the scale W_K to give true readings of the temperature for a black body, we measure only the colour temperature for a coloured body. If, however, we adjust the wedge W_R so that at some known temperature for a given coloured body, the wedge W_K reads this temperature, it will continue to indicate the true temperature for that body (with the same scale used for the black body), provided that the regions of the spectrum used are sufficiently narrow.

VIII.—MEASUREMENT OF THE AMOUNT OF OZONE IN THE EARTH'S ATMOSPHERE.

By G. M. B. Dobson, *D.Sc.*, and D. N. Harrison, *B.A.*

Read at Oxford, July 4, 1925.

Abstract.

The quantity of ozone present in the atmosphere has been measured by spectroscopic means on about a hundred days. A marked connexion with the pressure distribution at the surface, and particularly with the conditions at about 10 km., has been found.

OZONE has two strong absorption bands, one in the ultra-violet and one in the infra-red. It therefore absorbs some of the sun's radiation in addition to the earth's radiation. The ultra-violet absorption does not give appreciably increased radiative power, because the ultra-violet radiation of a black body at the temperature of the atmosphere is negligibly small. The equilibrium temperature of ozone is therefore higher than that of water-vapour or CO_2, which only absorb in the infra-red. It thus seems likely that variations in the amount of ozone might affect the temperature of the atmosphere in its neighbourhood—i.e., at great heights—and consequently the pressure at the earth's surface. It has been shown that there is no appreciable quantity of ozone near the surface, and all that there is, is probably above the troposphere.

The method used for measuring the ozone is a modification of that due to Fabry and Buisson. The ultra-violet absorption band of ozone begins at about 3,300 Å., and rapidly becomes stronger for shorter wavelengths, cutting off the sun's spectrum completely at about 2,850 Å. This region of the spectrum is photographed, and the intensities of a number of the Fraunhofer transmission lines are measured. Thus the difference in the absorption of any two wavelengths by the atmosphere is deduced. Before we can obtain the absorption coefficients we have to know the intensities of different wavelengths outside the atmosphere—i.e., before absorption; these are found by plotting the intensities as measured on the earth at different times of day against the distance through the atmosphere travelled by the rays, and extrapolating the curves to the point corresponding to zero distance. The difference of absorption of any two wavelengths is due partly to the different amount of scattering by air molecules and partly to the different absorption by ozone; the former effect can be allowed for, and hence the amount of ozone necessary to produce the remaining difference of absorption can be calculated. This may be expressed as the thickness which the ozone actually present would have if reduced to a layer of pure ozone at N.T.P., and the average value is about 3 mms.

Photographs are taken with a Féry spectograph, which has a special filter of bromine and chlorine in front of the slit to cut off all wavelengths longer than 3,300 Å., which would otherwise cause too much scattered light in the instrument. An optical wedge is placed immediately before the plate. Fig. 1 shows two photographs taken at about the same altitude of the sun, one on a day when there was little ozone, and the other on a day when there was a comparatively large amount.

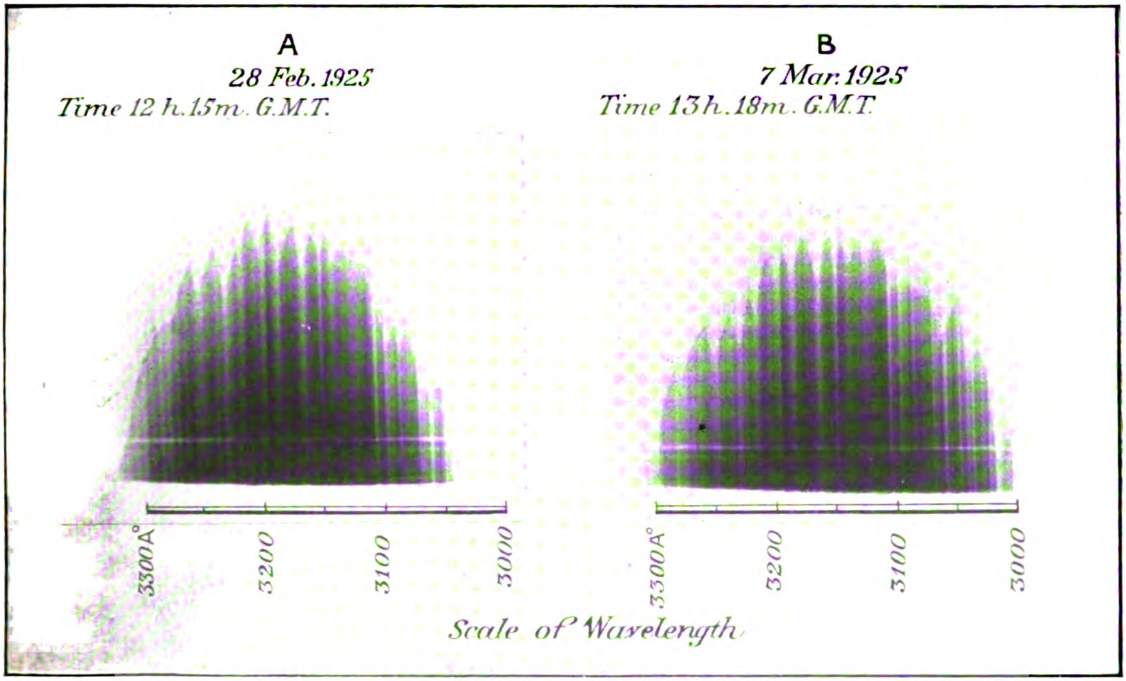


FIG. 1.

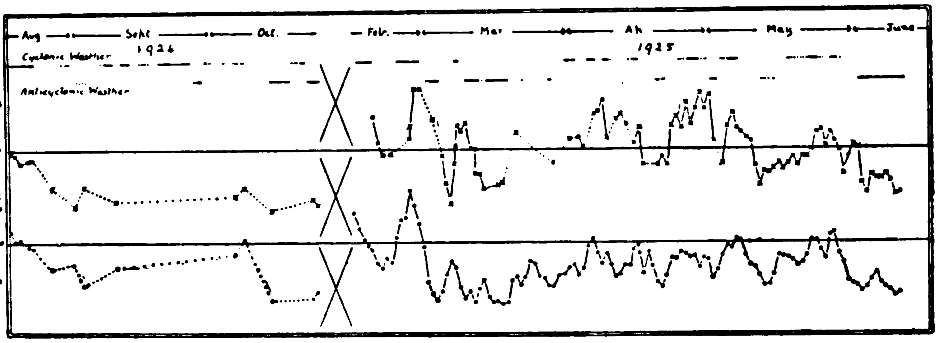
To face page **74**]

The heights of the lines are a measure of the intensities. It will be seen that the long wavelengths are about equal in the two cases, since there is practically no absorption by ozone. At the short wavelength end one photograph is much weaker than the other, owing to the absorption by the larger amount of ozone.

Fig. 2 shows the results of measurements, using the lines 3,232Å. and 3,052Å. The upper curve shows the amounts of ozone, in arbitrary units, on each day when observations were possible. The lower curve represents the daily values of the barometric pressure at Oxford (plotted inversely), and it is obvious that there is a correlation. The series of horizontal lines above refer to weather conditions; the upper ones show the occurrence of cyclones; and the lower, anti-cyclones. Dots mean that the conditions were not well marked. It will be seen that the amount of ozone tends to be low during an anti-cyclone and high during a cyclone, and that the maximum and minimum differ by about 50 per cent.

Other curves have been obtained, using other pairs of wavelengths, and these agree entirely with the one shown.

The sign of the correlation is that which would be expected, as an increase in the amount of ozone would tend to produce a higher temperature in the upper air, thus reducing the mass of air above the surface, and consequently the surface pressure.



[*Reproduced by kind permission of the Royal Meteorological Society.*]

FIG. 2.

It is further of great interest that the correlations with the pressure are much closer at great heights than at the surface. A fuller account has been published in the Quarterly Journal of the Royal Meteorological Society.

DISCUSSION.

Dr. C. CHREE: The subject of the Paper is of much interest to meteorologists. One thing we should like to know is the level where the ozone is found, whether at the top of the troposphere or at a higher level. It would be of much interest to have a comparison of corresponding daily values of ozone and of the "solar constant" as measured by Dr. Abbot and his collaborators.

Prof. W. F. G. SWANN: I should like to inquire as to the altitude, or rather the pressure, of the regions of the atmosphere to which the Paper refers. I am interested in this because I think there is some reason for supposing that the absorption of radiation by a gas at low pressure may be smaller than might be supposed at first sight. Presumably the energy becomes absorbed in the first instance in intermolecular transitions—the types of transitions associated with band spectra—and is only transferred to kinetic energy of translation at impact. The mean free time between impacts is of the order 3×10^{-10} seconds at atmospheric pressure. If the pressure were reduced to one hundredth of an atmosphere the time would be of the order 3×10^{-8} seconds. I is a matter of some interest to inquire whether a molecule could hold its energy for this length of time without falling back to its normal state through radiation. If it could not, then, at such pressures, many of the molecules would fail to convert the energy which they had absorbed into translation of kinetic energy, and would re-radiate it, so that to this extent the heating of the gas would be reduced. What the net result of this process would be is a matter for some speculation, but the problem of the effect of low pressures on heat absorption in gases is one not without interest. I presume, however, that the pressures to which the Paper refers are much higher than those which would be concerned in the phenomenon I have discussed.

Mr. L. F. RICHARDSON: This interesting application of laboratory method to the upper air shows that the pressure is correlated with the ozone content—a valuable new fact. It is, however, difficult to accept the authors' suggestion that the heating of the ozone may be the cause of the pressure change, for the ozone is not well placed for producing mechanical disturbances, being too high up. In the domestic hot water system the boiler must be placed low down. Sandström has called attention to the importance for meteorology of the level of heating, and recently H. Jeffreys (in a Paper read at the Royal Meteorol. Soc., May, 1925) has adjusted "Sandström's Theorem" in detail without, I think, diminishing its importance. So before accepting the authors' suggestion, which is so different from the Bjerknes view of cyclones, one would like to see a numerical calculation of the dynamical effects of heating the ozone. A more likely explanation of the correlation between ozone and pressure is that large masses of air have moved to Oxford from various latitudes; that both pressure and ozone-content have values characteristic of the radiation (waves or particles) of the latitude in which the air has recently wandered; and that during the journey to Oxford these characteristics, though changing, have not usually changed beyond recognition. This explanation is in accord with Goldie's investigation of temperatures and trajectories (A. H. R. Goldie, Quart. Journ. R. Meteor. Soc., January, 1923, p. 6).

Prof. A. FOWLER: I have been very much interested in this Paper. I recall that when Lord Rayleigh and I were investigating the absorption bands of atmospheric ozone in the spectra of the sun and stars some years ago, we were inclined to think that it might be possible to study the variations by comparing the intensities of the narrow absorption bands with those of adjacent groups of Fraunhofer lines. Such an investigation, however, called for more continuous observation than could be conveniently made in connection with college work, and we did not pursue the matter further. The method suggested by Dr. Dobson and Mr. Harrison seems to me very promising, though it was somewhat difficult to recognise the range of wavelengths observed in a hasty glance at the negatives on the screen, and a good deal may depend upon the choice of wavelengths to be compared. I was surprised to find that such large variations had been noted in the ozone absorption. Fabry and Buisson estimated the total amount of ozone ordinarily present to be equivalent to about 3 mm. thickness at atmospheric pressure, and the variations indicated by their observations were comparatively small. One of the most interesting questions connected with the atmospheric ozone is that of a possible variation with the 11-yearly period of the sun, depending upon a corresponding variation in the ultra-violet radiation. If the new observations are correct, it would seem that the direct effect of the solar variation is likely to be submerged by the large variations from day to day arising from other causes. I think that many besides myself will look forward to the opportunity of studying the details of the method and results when the Paper is printed.

IX.—THE ABSORPTION COEFFICIENT FOR SLOW ELECTRONS IN MERCURY VAPOUR.

By Robert B. Brode, *B.Sc.*, *Ph.D.*, Rhodes Scholar, Oriel College,
Oxford.

Read at Oxford, July 4, 1925.

Abstract.

The absorption coefficients of electrons having from 0·5 to 100 volts velocity were observed in the vapours of mercury, cadmium and zinc. Except for a small irregularity in cadmium, the absorption coefficient decreased uniformly with increasing velocity.

A MOLECULE has an effective area, due to its electric field, within which a passing electron will be deflected from its path. The total effective area of all the molecules in a cubic centimetre of gas at a pressure of 1 mm. of Hg is known as the absorption coefficient. If a beam of electrons is sent through a path length x in a gas at the pressure p, then

$$I = I_0\, e^{-\alpha x p}$$

where I_0 is the number of electrons in the beam at the beginning of the path, I the number which passed through the gas without being deflected, and α the absorption coefficient. This absorption coefficient has been observed for most of the common gases by Lenard and others.*

Apparatus.

The apparatus (Fig. 1) used in this experiment consisted of a filament F, two parallel discs D, and a ring R. The electrons were accelerated from the filament to the guard cylinders attached to the discs, and some of them continued on (to the ring) at uniform velocity, in the field-free space between the discs. The decrease in the number of electrons arriving at the ring when the mercury vapour was introduced was due to the deflection of those electrons that passed within the effective deflecting area of a molecule.

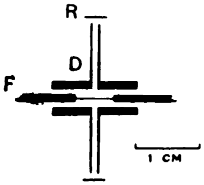


Fig. 1.

---

* **O. Lenard, Ann. der Phys., 12, 714 (1903). H. F. Mayer, Ann. der. Phys., 64, 451 (1921). C. Ramsauer, Ann. der Phys., 72, 345 (1923). R. B. Brode, Phys. Rev., 25, 636 (1925).**

The bulb containing the apparatus was of Pyrex glass. The metal parts were all made of nickel except the tungsten filament and the tungsten seals through the Pyrex. The apparatus was baked out for four hours at 550°C., and the nickel parts heated to a bright red heat by bombardment with 1,500 volt electrons from the filament. A small amount of mercury was distilled into the bulb, which was then sealed off from the vacuum pumps. After sealing off the bulb the pressure of the vapour could be determined from the temperature of the metal.

RESULTS.

The values of a were observed for electrons with velocities from 0·4 to 150 volts, as shown in Fig. 2. From 50 to 150 volts a decreased uniformly, from 22·5 at 50 volts, and 11·5 at 100 to 4·5 at 150 volts.

Above 100 volts the value of a is in good agreement with the values observed by Nettleton* for the effective area within which an electron must come to produce ionisation. From this it appears that the deflection of a high velocity electron also results in the ionisation of the molecule. The rate of increase of the effective area becomes less below 3 volts, but no indication was found of the maximum whose existence has been suggested by Minkowski.† The remainder of the curve above 3 volts agrees quite well with the theory given by Zwickey.‡ When the field acting on the electron is only that due to the polarisation which the electron itself causes in the molecule, the value of a varies as $K/V^{\frac{1}{2}}$, where K is a constant depending on the dielectric constant of a single molecule.

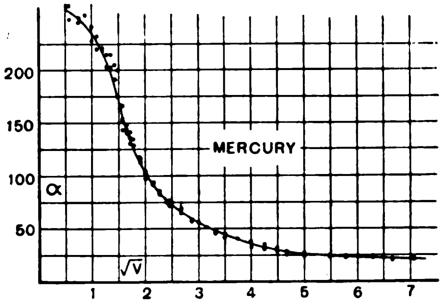


FIG. 2.

Since the reciprocal of the absorption coefficient is the free path of the electron at 1 mm. pressure, it will be seen that the free path is approximately proportional to the velocity. In problems of diffusion, where the velocity of the electron is not constant, the correct results will not be obtained with the assumption of constant free path.

A more complete account of this investigation of the absorption coefficient for mercury, together with observations on cadmium and zinc, will be published in the near future.

---

* L. L. Nettleton, Proc. Nat. Acad. Sci., 10, 140 (1924).
† R. Minkowski, Zeit. f. Phys., 18, 258 (1923).
‡ F. Zwickey, Phys. Zeit., 24, 171 (1923).

DISCUSSION.

Prof. E. N. da C. Andrade: Mr. Brode's Paper is very interesting, not only as confirming the surprising results obtained by Ramsauer with the inert gases, but as showing that other gases which are not monatomic can exhibit the same unexpected property—namely, that the absorbing cross-section, after increasing with diminishing velocity of the electron, reaches a maximum and then abruptly diminishes. We must therefore look for the explanation of this effect, not in the peculiar closed structure of the extranuclear electrons of the inert gases, but in some more general feature. In this connexion certain differences between Ramsauer's results and those of Mr. Brode are notewothy. Whereas for hydrogen and nitrogen Ramsauer finds that the absorbing cross-section increases as the electron velocity is indefinitely diminished to a constant value, which in the case of the former is a few times the gas-kinetic cross-section, and in the case of the latter very slightly exceeds the gas-kinetic cross-section, Brode finds both for them and for other gases an indefinite increase of cross-section down to the lowest velocities which he could employ. If these results are substantiated, it is possible that for all atoms and molecules there is a maximum, but that in the case of nitrogen, hydrogen and the others it occurs at such low velocities that it could not be demonstrated. Apart from a subsidiary maximum, probably attributable to a critical potential of the atom in that region of potential, Mr. Brode's curve for cadmium vapour(?) also shows an indefinite increase of absorbing cross-section, which again indicates that the difference between the curves for hydrogen and helium, say, is not due to the difference between a diatomic and a monatomic gas. Ramsauer's work has not, in my opinion, received sufficient attention, and I am very glad that it is being extended in this country. The explanation of the maximum is not easy, and, in spite of the attempts of Hund and others, it may be said that it is still to seek. When it comes it will probably throw some light on the problem of atomic structure.

Dr. G. W. C. Kaye: The author has fully realised that for useful measurements to be made it must be possible to eliminate completely all foreign matter and to be able to isolate the tube completely as occasion requires. I am much taken with the very neat device by which the closing stopper can be controlled at will by the heating and expansion of the supporting steel wire.

X.—TWO NEW TYPES OF HIGH VACUUM GAUGE.

By E. Bolton King, Duke of Westminster Research Student of Christ Church, Oxford.

Read at Oxford, July 4, 1925.

Abstract.

Descriptions are given of a new type of decrement gauge in which the individual oscillations are photographed, and a variation of the Pirani gauge, in which no metal is exposed to the vacuum.

THE first gauge is of the decrement type, depending for its action on the variation of viscosity with pressure when the latter is such that the mean free path of the gas molecules is of the same order as the dimensions of the apparatus. The essential part consists of silica fibre *A* (Fig. 1), between 3 and 4μ in diameter and 4 cms. long, which is fixed by a small amount of gold to the silica frame *B*, the tension, which thus does not vary with changes in temperature, being about half that required

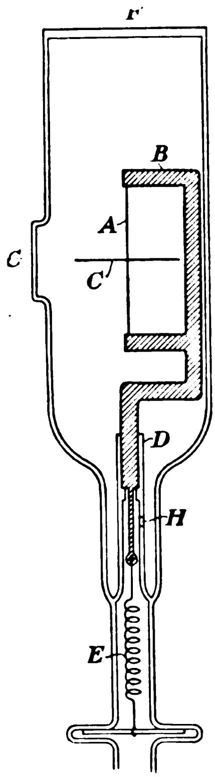


Fig. 1.—Diagram of Decrement Gauge.

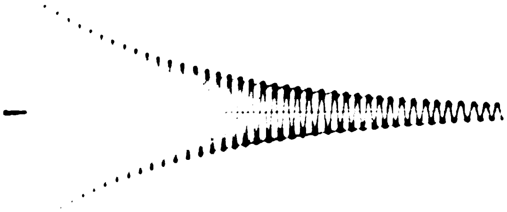


FIG. 3.—TYPICAL PLATE OF DECREMENT GAUGE.

[*To face page* **81**

for breaking. At the centre of this fibre, and at right angles to it, are fixed two 10μ fibres 2·5 cms. long, one on either side of the suspension. The ends of these remote from the frame are fused into a sphere about 50μ in diameter, while the other ends are fixed together by a minute amount of iron, which when activated by an electro magnet outside the case also serves to start the oscillations of the cross-piece, the damping of which is measured. If the external case is of glass, the frame is held in the cylindrical socket *D* by the spring *E*, while if it is of silica the frame is fused directly to it. Two flat windows, *G* and *F*, are fused to the case, the former for observing and the latter for illuminating the tip of the cross-piece. The gauge is connected to the other apparatus at *I*, communication with the interior being through the hole *H*.

The advantages of this gauge are :—

(1) The period of oscillation of the cross-piece is of the order of 1 sec., which is much longer than that of the usual type of quartz fibre gauge, in which a single fibre about 100μ thick and some cms. long is clamped rigidly at one end and the oscillations of the free end observed. Hence, instead of taking the time for the amplitude of the oscillations to fall to a certain fraction, and so calculating the damping, a record of all the oscillations can be obtained photographically. This was done by the method shown in Fig. 2. Light from the lamp *S* is focused by the lens *L* on to the tip of the pointer *A*. This acts as a convex mirror of very large curvature, and by means of the microscope objective *O* a small image of the lamp is formed on the photographic plate *P* after reflection in the right-angled prism *R*. This prism is slowly rotated during the oscillations by a clockwork motor driving through a worm and cog, with the result that damped oscillation curves of the type shown (Fig. 3) are produced on the plate.

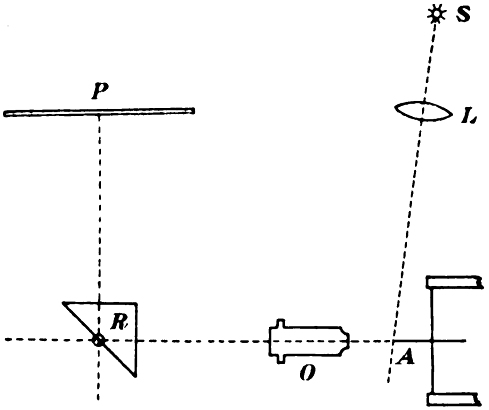


Fig. 2.—Diagram of Optical System for Decrement Gauge.

(2) The second advantage of the gauge is that the plane of vibration cannot change as in the usual quartz fibre gauge,* and thus the true decrement is always obtained. If by chance the cross-piece oscillates in itself, the fact is easily discernable on the plate.

(3) The zero is fixed and the oscillations are not disturbed by external vibrations

---

* Zeits. f. Electrochem., 20, 296 (1914) ; Phil. Mag., 47, 32 (1914), and other Papers.

as in the decrement gauges of Sutherland* and Hogg,† or the Knudsen gauge in any of its various forms.‡

(4) The gauge, especially the type with a silica case, contains very few metal parts, the presence of which may give rise to considerable absorption of gas at low pressures.

The theory of the gauge is the same as for all types of decrement gauge—viz., the relation between the damping and the pressure is given by the equation

$$d=KP\sqrt{\frac{M}{T}}$$

where d is the damping, P the pressure, M the molecular weight of the gas present, T the temperature and K a constant depending on the dimensions of the instrument. In the case where several gases are present, the sum of a number of terms must be taken corresponding to the partial pressures of the various constituents, and we have an equation of the type

$$d=\frac{K}{\sqrt{T}}(P_1\sqrt{M_1}+P_2\sqrt{M_2}+\ .\ .\ .)$$

The instrument is not absolute, but must be calibrated against known pressures. These were obtained by connecting it to a large volume (about 2,000 c.c.), in which small bulbs containing a known amount of gas could be broken by electromagnetic hammers, thus producing known small pressures. These bulbs varied in volume from 0·1 to 0·01 c.c., and, having been accurately calibrated, were filled at a pressure of between 3 and 5 cms. of mercury, which pressure could be measured with a mercury monometer with a very small error.

In calibration, the whole apparatus was exhausted and heated to about 300°C. for some hours till it became quite hard. Pure dry oxygen was then let in to about 2 cms., and after being allowed to stand over night it was pumped out without extra heating. This method was adopted, since the baked out walls of the glass were found to absorb the gas during calibration, while if they were saturated with the gas which was about to be used this phenomenon did not occur. The apparatus was then sealed off from the pumps and the bulbs containing oxygen broken one by one .

When the apparatus is fully exhausted there is still a small damping d_0 of the oscillations, due to the residual gas and the actual damping of the quartz fibres, which reduces the amplitude to half value after about 500 complete swings. Since this is always about the same, the latter cause is probably predominant. The figures of a typical calibration with oxygen are as follows :—

$P\sqrt{M}10^4$ P in mms. of Hg	d	$d-d_0$	$\frac{d-d_0}{P\sqrt{M}}$
0	1·00104	……	……
14·60	1·00173	0.00069	0·472
34·58	1·00262	0·00158	0·457
54·99	1·00369	0·00265	0·482
76·37	1·00463	0·00359	0·472
100·77	1·00580	0.00476	0·472
125 50	1·00710	0·00606	0·482
150·69	1·00822	0·00718	0·476

When these points are plotted they all fall practically on a straight line (Fig. 4).

---

* Phil. Mag., 43, 83 (1897).

† Proc. Am. Acad., 42, 115 (1906), and 45, 3 (1909).

‡ Ann. Phys., 44, 525 (1914) ; Ann. Phys., 41, 1 (1913), and other Papers.

Fig. 5 gives points obtained for another instrument, when calibrations were made with three different gases—oxygen, argon and carbon dioxide—and shows that the $P\sqrt{M}$ law is true. The relation was linear for this gauge for values of $P\sqrt{M}$ up to about 0·125 [P in cms. of Hg], which corresponds to a pressure of oxygen of $2 \cdot 10^{-3}$ mm. The lower limit of the gauge for light gas, such as oxygen, is $2 \cdot 10^{-6}$ mm., while for a heavy gas, such as mercury, is $1 \cdot 10^{-6}$ mm.

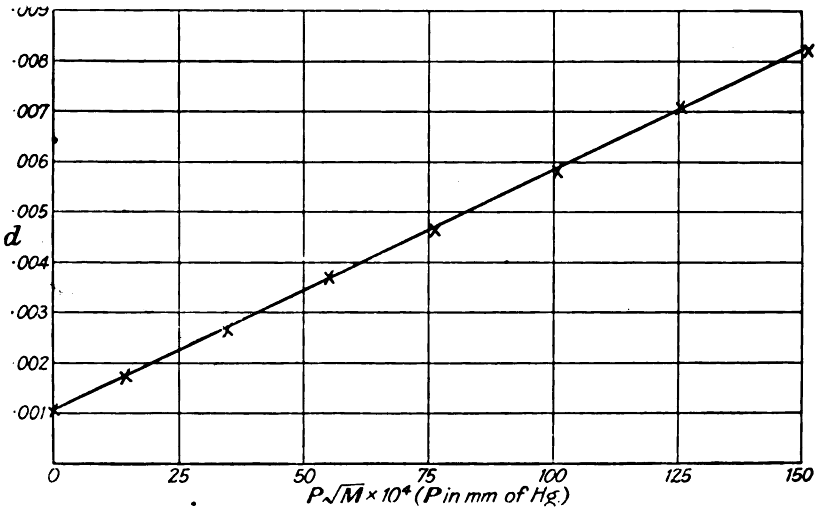


FIG. 4.—CALIBRATION CURVE OF DECREMENT GAUGE.

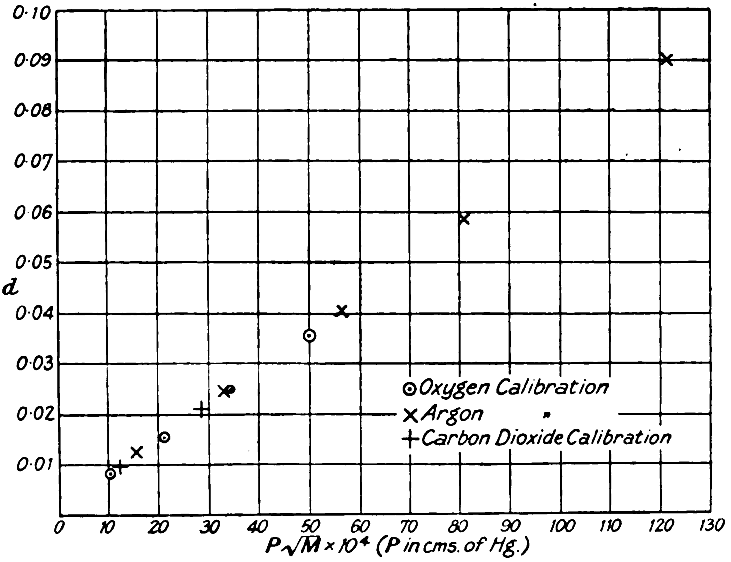


FIG. 5.—CALIBRATION CURVE WITH VARIOUS GASES.

Owing to the fact that any metal in a gauge may absorb or give out gas, thus invalidating results, and also for use with active vapours, it is desirable to have a gauge which contains no metal exposed to the gas. For this purpose a modification of the Pirani gauge* has been made. This gauge depends for its action on the fact that, as the pressure changes the heat loss from the hot filament to the walls changes. Thus, if the current in the filament is constant, the temperature and therefore the resistance changes. In the modification described the filament is replaced by a spiral glass capillary tube *A* (Fig. 6), whose internal diameter is from 10 to 20μ, external diameter from 100 to 200μ, and total length, when unwound, about 100 cms. This spiral ends in the larger tubes *BB*, which are held together by the glass rods *CC*, which hold the whole rigid when it is being sealed into the outer case. The spiral and the tubes *BB* are then filled with mercury and form a conducting filament with a glass surface. The resistance of the gauges made varies from 300 ohms to 1,700 ohms. In practice the gauge is placed in one arm of a Wheatstone bridge, which is balanced when the filament is at about 30°C. above the temperature of the case, which is kept in a thermostat. The voltage which must be put across the bridge in order to keep it balanced is then used as a measure of the pressure. These gauges have not yet been carefully calibrated, but a typical one of 1,562 ohms resistance, with the filament at 44°C., needed 15 volts across the bridge at a pressure of about 0·2 mm. To keep the bridge balanced at a pressure of about $5 \cdot 10^{-4}$ mm. this potential had to be reduced to 5 volts. The sensitivity would thus seem to be as great as other Pirani gauges, and equilibrium is reached within 30 seconds of switching on the current. It is hoped that a fuller account of these gauges may be given later.

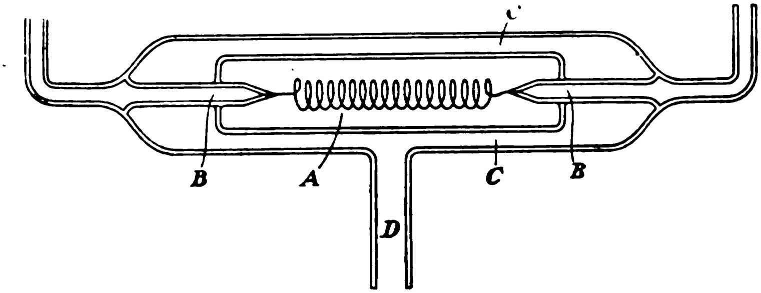


Fig. 6.—Diagram of Modified Pirani Gauge.

In conclusion I must express my deep gratitude to Prof. Lindemann for originally suggesting the two gauges, and to both him and Mr. T. C. Keeley for their continual help and advice.

NOTE ADDED DECEMBER 1, 1925.

In the latest decrement gauge with a glass case the cylindrical socket *D* is replaced by a fused silica-glass joint. The metal spring is then not needed.

DISCUSSION.

Dr. G. W. C. Kaye: Mr. King has shown us two or three devices which are likely to be of value to the worker on high vacua. In his first device the author has developed a neat technique for recording the damping by what might be described as an adaptation of Threlfall's gravity balance. The method of measuring the pressure in an enclosure by sharing with it the contents of "capsules" of gas of known amount is a useful means of avoiding the use of the McLeod gauge. As regards the mercury-in-glass-filament Pirani gauge, I wonder whether one of the most useful features of the metal-filament Pirani gauge—that of very quick response—would not be largely nullified. In my own work with metal-filament lamp Pirani gauges connected to a discharge tube I have had trouble from electrostatic effects, and I imagine that these effects would still persist with the author's type of instrument.

---

* Trans. Am. Electrochem. Soc., 20, 243 (1911).

XI.—AN APPLICATION OF SPECTRO-PHOTOGRAPHY TO THE MEASUREMENT OF HIGH TEMPERATURES.

By I. O. GRIFFITH, *M.A.*

Read at Oxford July 4, 1925.

ABSTRACT.

The spectrum of the source is photographed through a neutral wedge placed immediately in front of a photographic plate. The curved boundary of the spectrum varies in height, the variation depending upon the distribution of energy in the source—i.e., upon its temperature. It is assumed that the source radiates as a black body or a grey body, but with certain limitations the method is applicable to bodies which are neither black or grey.

IN this note is described an application of photography to the accurate determination of the temperature of a luminous body. The temperature of such a body can be determined from a knowledge of the ratio of the radiation intensities corresponding to any two wavelengths in its spectrum. Various methods are available for measuring these intensities, but for a source which is difficult to maintain in a steady state for any length of time, such as the one which the writer has been investigating, a photographic method, permitting an almost instantaneous record of the spectrum of the source, is extremely convenient.

If for a source at temperature T, E_λ denotes the intensity of radiation of wavelength λ falling on the receiving instrument, in our case a photographic plate, we may write

$$E_\lambda = a_\lambda \, . \, \varepsilon_\lambda \, . \, \varphi(\lambda, T) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

a_λ is the absorption coefficient for wavelength λ of the various lenses and prisms which the radiation traverses in its passage from the source to the plate, and ε_λ represents the emission coefficient of the radiation for wavelength λ. For black or grey body radiation, ε_λ is a constant depending on the degree of greyness of the body and $\varphi(\lambda, T)$ represents Planck's function.

For another wavelength λ'

$$E_{\lambda'} = a_{\lambda'} \, . \, \varepsilon_{\lambda'} \, . \, \varphi(\lambda', T)$$

and

$$\frac{E_\lambda \, . \, d\lambda}{E_{\lambda'} \, . \, d\lambda'} = \frac{a_\lambda \, . \, \varepsilon_\lambda \, . \, \varphi(\lambda, T)d\lambda}{a_{\lambda'} \, . \, \varepsilon_{\lambda'} \, . \, \varphi(\lambda', T)d\lambda'}$$

If we have a comparison source at a known temperature, T_s, then

$$\frac{S_\lambda \, . \, d\lambda}{S_{\lambda'} \, . \, d\lambda'} = \frac{a_\lambda \, . \, \varepsilon_\lambda \, . \, \varphi(\lambda, T_s)d\lambda}{a_{\lambda'} \, . \, \varepsilon_{\lambda'} \, . \, \varphi(\lambda', T_s)d\lambda'}$$

where S_λ denotes the radiation intensity for wavelength λ of the comparison source, a carbon arc at atmospheric pressure.

Hence

$$\frac{E_\lambda d\lambda}{E_{\lambda'} d\lambda'} \div \frac{S_\lambda d\lambda}{S_{\lambda'} d\lambda'} = \frac{\psi(\lambda,\lambda',T)}{\psi(\lambda,\lambda',T_s)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where $\psi(\lambda,\lambda',T)$ has been written for $\dfrac{\varphi(\lambda,T)}{\varphi(\lambda',T)}$

The dispersion $d\lambda$ and absorption a_λ of the apparatus intermediate between the source and the receiving instrument have been eliminated. It will be noticed that the emission characteristic of the source represented by ε_λ has also disappeared, so that the method is applicable to the determination of the temperature of non-black bodies.

For the measurement of the ratio of radiation intensities of various wavelengths, the photographic intensities as measured by the density of the photographic image are reduced to absolute intensities by means of a neutral wedge,* as suggested by Merton and Nicholson.†

The light from the source is arranged to fall on the slit of a spectograph, so that its intensity in a direction parallel to the length of the slit is constant. In front of the spectrometer slit or in contact with the photographic plate is placed the neutral wedge with its lines of equal density parallel to the dispersion of the spectograph, the absorption of the wedge increasing uniformly in a direction parallel to the slit.

The law of absorption of the wedge is given by

$$E = E_0 . 10^{-Ky} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

y being the distance measured parallel to the slit between two points corresponding to intensities E, E_0 in the light transmitted through the wedge. The value of the constant K which has been found convenient in practice is 1·5 or 3 per centimetre, according as the wedge is near the photographic plate or in front of the spectrometer slit.

The image of the source as it appears on the plate is shown in Fig. 1, the intensity along any ordinate decreasing uniformly in density from top to bottom. The curved boundary of this spectrum varies in height, as measured from the reference line, the variation depending upon the distribution of light in the source, the absorption in the apparatus including the wedge, the dispersion of the spectograph and the colour sensitivity of the plate. Every plate is standardised by photographing on each plate the spectrum of the comparison source.

After development, the image densities are measured and the distances from the zero line to the points where the density has a certain fixed value are recorded, so that for any given wavelength we know the value of y corresponding to a certain value of log E and

$$\log E = \log E_\lambda - Ky \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

---

* The wedge consists either of a wedge-shaped piece of neutral grey glass cemented to a similar piece of clear glass to form a parallel plate, or of a very thin wedge of neutral grey gelatine between glass plates.

† Phil. Trans., A, Vol. 216, p. 459, and Phil. Trans., A, Vol. 217, p. 237. During the course of the investigation a Paper by Plaskett has been published [publications of the Dominion Astrophysical Observatory, Victoria, B.C., Vol. 11, No. 12], in which a similar method is described in connexion with work in astronomical spectrophotometry.

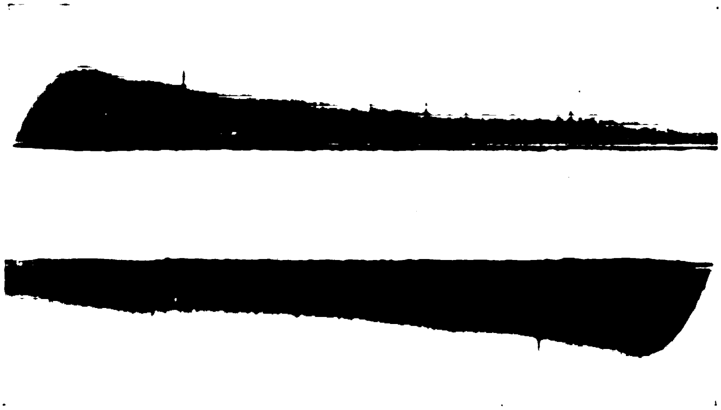


FIG. 1.

To face page 86]

In the same way, for the comparison source which is recorded on the same plate

$$\log E = \log S_\lambda - Ky_s \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\therefore \; \log \frac{E_\lambda}{S_\lambda} = K(y - y_s) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

It will be noticed that no characteristic of the plate or of its treatment enters into this equation, and that E_λ and S_λ are measured in terms of a constant intensity E, under the one condition that equal intensities of light of the same colour give equal densities on the same plate.

The actual values of y measured are the distances from the reference line, but as we are only concerned with differences, the fact that the reference line may not actually be the line of zero density of the wedge does not matter.

We may write equation (2) in the form

$$K(y - y_s) - K'(y' - y_s') = \log \frac{\psi(\lambda, \lambda', T)}{\psi(\lambda, \lambda', T_s)} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The y ordinates are measured on a photometer designed by Mr. G. M. Dobson,* in which the sensitive element is a photo-electric cell connected through a high resistance to a sensitive quick period string electrometer.† Variations in the source of illumination and in the voltage applied to the photo-electric cell are eliminated. The density of the background or unexposed parts of the plate is automatically allowed for, and all densities can be measured with equally good accuracy.

As the light does not necessarily fall on the wedge as a parallel pencil, it is essential that the measurement of the wedge constants K and K' should be carried out when the wedge is in its actual position in the instrument. A constant source of light—viz., a tungsten filament focus bulb—is placed in the position previously occupied by the luminous source whose temperature is being measured. The intensity is reduced in a definite ratio by interposing in the parallel part of the beam a perforated gauze, which is rotated in order to eliminate the effect of any irregularities in the perforations. Two photographs of the source are taken on a single plate, one with and one without the perforated gauze. After each exposure and before the plate is removed from the spectograph, a helium tube is placed in front of the slit and the lines of its spectrum serve as reference lines. Within the spectral range which is utilised (4,000 Å. to 7,000 Å.) the values of K are constant—i.e., the wedge is neutral—and in practise a mean value of K of 1·46 per cm, has been taken as correct over the effective portion of the spectrum, the wedge being placed in contact with the plate.

The y ordinates of an image such as that shown in Fig. 1 can be measured with a probable error of 1/20 mm., so that the probable error in the expression on the left-hand side of equation (7) is 1/10 mm. This corresponds to a probable error in temperature of approximately 40° at 5,000° and 150° at 10,000°.

---

* Proc. Roy. Soc.

† Lindemann and Keeley, Phil. Mag., 47, March (1924).

XII.—ON THE BENDING OF CRYSTALS.

By C. H. Bosanquet.

Read at Oxford, July 4, 1925.

IT was observed by Coblenz in 1903* that slips of rocksalt immersed in strong brine at 50°-70° could be plastically bent. This phenomenon was mentioned by R. W. Wood at the British Association meeting in 1923, and has recently been investigated by Joffé. Experiments in this laboratory show that slips about 15 × 5 × 1-2 mm. can be bent into a semicircle in hot water or hot brine.

The distortion may be due to one of three causes :—

(*a*) There may be irrotational slip along cleavage planes, all portions of the crystal remaining parallel to their original direction.

(*b*) There may be alteration in the spacing of the crystal lattice, as in the elastic bending of a rod.

(*c*) The large crystal may break down into a number of small undistorted crystals, each of which makes a small angle with its neighbours. In this case the prismatic spaces between crystals would presumably be filled with NaCl in an amorphous state.

As regards the first possibility, of irrotational slip, the ends of the specimen appear to remain perpendicular to the other faces in their vicinity, instead of parallel to each other, and this is also true of the general direction of cleavage if a specimen is broken in half. The broken ends are not in general flat, but quite appreciably cylindrical.

If the second supposition is true, and bending entails changes of the interatomic distances without change of neighbours by the individual atoms, it is difficult to see why the slip should not straighten elastically as soon as the forces are removed.

The third possibility, that of breaking down into undistorted microcrystals, thus appears most likely, and it is also favoured by the curvature of the fractured surfaces.

These theories have been tested by X-ray reflexion. In Fig. 1 *C* is the crystal, *P* the plate, *S* a lead screen with a wide slit. The anticathode acts sufficiently well as a line source without the use of any narrow slits. *DB* is the direct beam throwing a shadow of the crystal on the plate, and *RB* is the reflected beam. During an exposure the crystal was rocked through an angle of about 10° to ensure that all portions passed through their reflecting angle.

Owing to the small area of the reflecting faces and the large angle through which the crystals were rocked, most of the reflexions, though perfectly clear on the negatives, were too faint for reproduction, and all the figures are taken from tracings of the negatives.

---

* Phys. Rev. (1903).

Fig. 2 shows the α and β lines of Mo reflected from a curved crystal, and the position of the axis of rotation is shown dotted. If the curvature were due to irrotational slip, the reflected lines should have exactly the same size and shape as the upper edge of the shadow, whilst actually they are at least twice as long. This indicates that the orientation of the lattice varies from one part of the crystal to another.

Fig. 3 (A and B) are tracings of two reflexions from broken ends of curved crystals; A was so faint that only the α line was visible. The fact that the reflected lines are arcs, instead of short lines of length about equal to the diameter of the anticathode, shows that considerable variations of orientation occur among the microcrystals in a single cross-section, as was to be expected from the shape of the fracture. The arcs also are portions of circles with centres at the shadow of the reflecting face, indicating that within the limits of measurement, or rather less than 1 per cent., the longitudinal spacing of the atomic planes is the same along both inner and outer edges of the curve. With the same accuracy the radii of the arcs agreed with the distance between direct and reflected beams obtained with an unbent crystal.

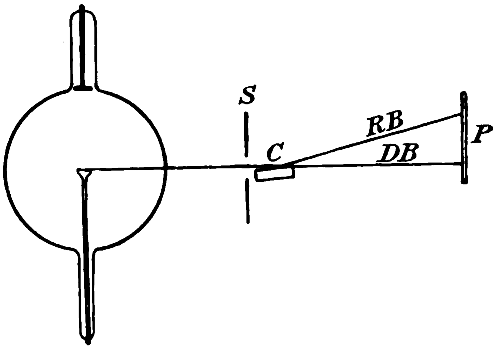


FIG. 1.

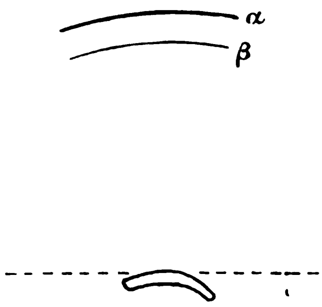


FIG. 2.

In fact, no crystal gave any reflexion which indicated a change in the lattice constant, in spite of the fact that the radius of curvature was only of the order of five times the thickness.

Fig. 4 shows the effect with an unbent crystal. Owing to the fact that the lines were not lengthened by distortion, the intensity is much greater in this case, and all four lines in the *K* spectrum of Mo appear. The length of the lines is entirely accounted for by the geometry of the apparatus.

The crystals used in the photographs of Fig. 3 were also rotated through 90°, so that reflexions were obtained from their edges, the plane of incidence being roughly parallel to the tangent planes of the curved surfaces. The results were indistinguishable from Fig. 4, showing that planes parallel to the plane of bending remain sensibly unwarped.

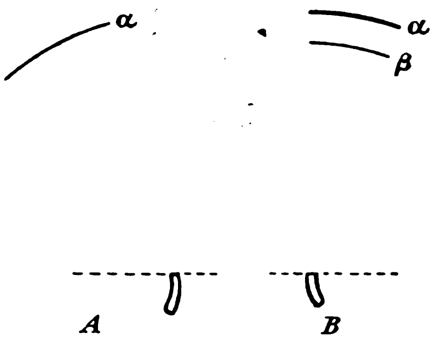


FIG. 3.

Fig. 5 shows the effect of limiting the width of the beam by means of a vertical slit. Only the shaded portion of the crystal was illuminated, and the shortness of the lines indicates that the microcrystals over a small area of the face are sensibly parallel to each other.

These conclusions are in general agreement with the work of Joffé.* He is of the opinion that the process of bending consists of the breaking down of the crystal into small units, which slip along rhombododekahedral planes, and in addition turn through various angles. He makes no suggestion, however, as to what is the substance filling up the irregular spaces left between the crystals.

FIG. 4.

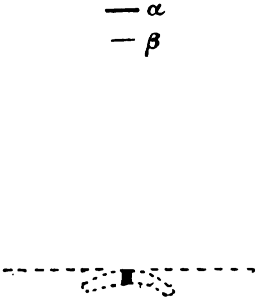


FIG. 5.

---

* Zeit. fur Phys., 22.

The slip, then, behaves as if it consisted of a number of small perfect crystals embedded in a very viscous fluid, presumably amorphous NaCl. The action of the hot liquid in bending is probably the prevention of the formation of cracks. If a minute fissure forms it will immediately be filled with NaCl solution saturated with respect to plane surfaces, and supersaturated with respect to concave surfaces, so that solid will be deposited in the crack at the point of maximum stress. The result of this will be that the tensile strength will be enormously increased. Joffé and Lewitsky * find that the tensile strength of a certain specimen was 450 g. per square mm. dry, and more than 4,000 in water, the elastic limit being 920 g. per square mm. The tensile strength when dry is independent of temperature, and the elastic limit decreases with temperature until they become equal at about 200°.

These results all appear to be in accordance with the theory outlined above.

---

* Zeit. fur Phys., 31 (1925).

DEMONSTRATION OF THE KINETIC PROPERTIES OF A GAS JET.

By Dr. J. S. G. Thomas.

THE demonstration was designed to illustrate the Bernoullian property of a gas jet, which has a central region of low pressure. Gas discharged through a large orifice from a gas cylinder was employed.

(*a*) The jet was directed downwards on to a plate, and it was shown that a ping-pong ball, instead of being blown away when placed on the plate, takes up a position of stable equilibrium at the centre of the jet. The stability was demonstrated by inclining the plane on which the ball was supported: a considerable inclination fails to dislodge the ball. When brought near the orifice the ball flies up to this and adheres to it.

(*b*) The jet was directed upwards and a toy balloon thrown into it. The balloon then rested in stable equilibrium at a considerable height above the jet, and the equilibrium persisted even when the jet was inclined to the vertical. On insertion of the operator's hand into the jet so as partly to shield the balloon, the latter appeared to be attracted towards the hand; this phenomenon afforded an illustration of Le Sage's theory of gravitation.

Physics Lib.

MAR 9 1926

THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 38.—PART 2.

FEBRUARY 15, 1926.

Price to Non-Fellows **6s.** *net, post free* **6/3.**

Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
FLEETWAY PRESS, LTD.,
3-9, DANE STREET, HIGH HOLBORN, W.C.1.

1926.

THE PHYSICAL SOCIETY OF LONDON.

1925-26.

OFFICERS AND COUNCIL.

President.

F. E. SMITH, C.B.E., F.R.S.

Vice-Presidents.

(WHO HAVE FILLED THE OFFICE OF PRESIDENT)

SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, M.A., LL.D., F.R.S.
SIR ARTHUR SCHUSTER, PH.D., Sc.D., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. VERNON BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E., M.A., F.R.S.
ALEXANDER RUSSELL, M.A., D.Sc., F.R.S.

Vice-Presidents.

C. R. DARLING, F.I.C.
D. OWEN, B.A., D.Sc.
E. H. RAYNER, M.A., Sc.D.
J. H. VINCENT, D.Sc., M.A.

Secretaries.

PROF. A. O. RANKINE, D.Sc.
Imperial College of Science and Technology, South Kensington, S.W.7.

J. GUILD, A.R.C.Sc., D.I.C., F.Inst.P.
Lalbagh, Park Road, Teddington, Middlesex.

Foreign Secretary.

SIR ARTHUR SCHUSTER, PH.D., Sc.D., F.R.S.

Treasurer.

R. S. WHIPPLE.
45, Grosvenor Place, London, S.W.1.

Librarian.

J. H. BRINKWORTH, B.Sc.
Imperial College of Science and Technology.

Other Members of Council

G. B. BRYAN, D.Sc.
D. W. DYE, B.Sc.
A. FERGUSON, M.A., D.Sc.
F. L. HOPWOOD, D.Sc.
E. A. OWEN, B.A., D.Sc.
R. W. PAUL.
J. ROBINSON, M.Sc., PH.D.
J. S. G. THOMAS, D.Sc.
W. S. TUCKER, D.Sc.
PROF. A. M. TYNDALL, D.Sc.

Assistant Secretary (Publications)

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley, N.3.*

XIII.—ATOMIC DIMENSIONS.

By R. G. LUNNON, *M.A.*, *M.Sc.*

Received September 29, 1925.

(*Communicated by* PROF. A. O. RANKINE.)

ABSTRACT.

The Paper deals with the diameters of the atoms of the elements, and compares the estimates obtained by various methods—viz., (1) Atomic volumes; (2) X-ray analysis; (3) Viscosity of gases; (4) Van der Waals' equation and its modifications; (5) Compressibility; (6) Viscosity of liquids; (7) Viscosity of solutions; (8) Diffusion of ions; (9) Mobility of ions in solutions; (10) Latent heat of solution; (11) Speculations as to atomic laws of force; (12) Scattering of X-rays; (13) Bohr's theory in the case of the hydrogen atom; (14) Ionisation potentials; (15) Band spectra; (16) Chemical constant; (17) Optical rotation; (18) Molecular films; (19) Langevin's theory of diamagnetism; (20) Impacts of a stream of electrons on gas molecules; (21) Density changes in permutite; (22) Melting points of solids.

The results obtained by these methods, of which an extensive bibliography is given, are fairly accordant, and their mean shows that the addition of an inner electron shell gives an increase in diameter of roughly 0·5Å.

ESTIMATES of atomic and molecular dimensions have now been made in upwards of thirty different ways, and it is the purpose of the present Paper to collect and compare their results. The atomic volumes and X-ray crystal data will be considered first; next the many other methods, each of which is applicable to a few elements only; and finally the results of these methods are compared, taking the elements in groups. The results are shown graphically in each case, and a complete discussion of their relative merits is omitted, for brevity. Complete references are given at the end of the Paper, and a fuller comparison of some of the methods may be found in a summary by Herzfeld.(0)

The most extensive contribution to this subject has been the application of X-ray crystal analysis, and a partial summary of its results has been given by W. H. and W. L. Bragg.(1) In two different curves, the values of the "atomic radii" or "radii of combination," have been given for a large number of elements, and the parallel between these and the atomic volumes has been suggested. It is of value to re-state first the data of the Lothar Meyer curve of atomic volumes. The volume available for each atom of an element is easily calculated when the density of the element is known, and the cube root of this quantity is a measure of the diameter to be ascribed to the atom, if the atoms were packed as cubes, or as spheres in a simple cubic lattice. These figures have been re-calculated, and are presented in a new form (similar to that of the curves given by Davey(2)) in Fig. 1. The arrangement of the elements in steadily increasing atomic number is broken so as to give the same abscissa to all elements of the same group; this means that the cube root of the atomic volume is plotted against the valency, with a special extension for the long periods. The value of this method is that it shows very clearly the regularity of the variation in atomic dimensions—a regularity which has greatly improved as more reliable data have become available. Of the 90 known elements, 18 have not been measured, and all the rest except two (nitrogen and arsenic) follow the rule of increasing in " size " within their groups and are recorded in the figure. The curves cross each other only on the rare earth branch, when these two are omitted.

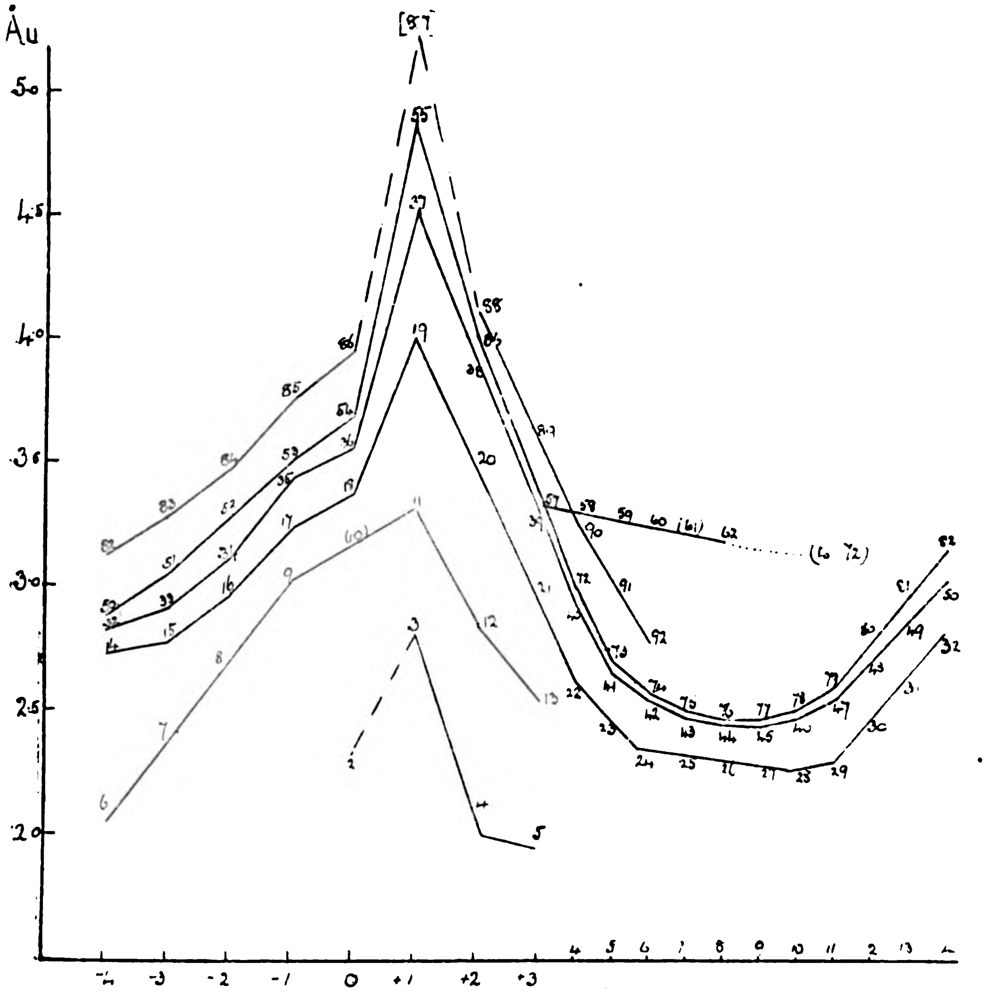


FIG. 1.—CUBE ROOTS OF ATOMIC VOLUMES.

In some parts of the curves the curves are exactly parallel. Biltz[(3)] has pointed out that the two following relations hold for consecutive elements :—

1. Atomic vol. of halogen = 0·8015 × at. vol. of rare gas.
2. Atomic vol. of alkali = 1·823 × at. vol. of rare gas — 6·10.

The figures are certainly not final, chiefly because they are derived from densities measured at various temperatures. Pierucci,(4) in pointing out that the density at the absolute zero should alone be used in these calculations, estimated that reliable data could only be given for 29 elements. Some careful estimates of " zero density " values have since been made by Herz,(5) using Lorenz's formulæ, and these we have included in our data, which therefore differ from the best earlier table, that prepared by Stefan Meyer(6) in 1915.

It is easy to pass from the volume of the space occupied by each atom to the volume of the atom itself, if the shape of the atom is assumed and the type of atomic packing is obtained by the methods of crystal analysis. Assuming a spherical atom, a fraction(7) 0·52 of the total space is taken up by the spheres if the lattice structure is a simple cubic one, 0·68 for a body-centred cubic lattice, and 0·74 for a tetrahedral or a face-centred cubic. It follows that the data of Fig. 1 can be used to give the atomic diameters, for the figures need, e.g., to be multipled by $\sqrt[3]{0{\cdot}68/0{\cdot}52}$ or by $\sqrt[3]{0{\cdot}74/0{\cdot}52}$—i.e., by 1·09 or 1·12—according to the crystal lattice. The curve of atomic diameters must therefore be similar to that of Fig. 1, for although the different types of lattice do not occur with a regular variation through the groups of elements, yet the difference between the factors for different lattices is very small. The actual results of X-ray crystal analysis are given by the curves of Fig. 2, and their shape confirms the above indication.

The assumption of sphericity in the atoms is unnecessary in the X-ray analysis, and the figures refer to the distance of nearest approach of two atomic centres, and this corresponds to a diameter. Only 40 of these are as yet available for elements in the crystalline state ; they have been collected by Bragg,(1) Wyckoff,(8) Davey(9) and Scott.(10)

There are hardly any data of this kind for electronegative elements, and estimates of their size have to be made from polar compounds.(11) In these it is now clear that the atom does not behave as though it were a sphere of constant size ; the space which it occupies, as an ion, depends upon the other elements with which it is combined. The atomic radius is not exactly an additive property in compounds. This is particularly clear in the complete set of figures for the alkali halides given by Havighurst,(12) for which an accuracy of one-tenth per cent. is claimed. It is sometimes useful, however, to retain the idea of the spherical ion, and Bragg retains the term " radius of combination." What is actually measured is the distance between the centres of two neighbouring ions of different kinds, and further deductions involve further hypotheses. Examples of two different views at this point are given by Bragg and by Davey, and Fig. 2 contains both sets of results.

For the most part, these curves run in rough similarity with those of Fig. 1. There is a striking difference, however, in the rising arms, for crystal data assign to the ions of the sulphur group elements and to the halogens a very much lower diameter than would follow from the atomic volume figures. This is probably due to the atom sharing electrons with its partner in the compound, and so approaching it more closely.(11) For the electro-positive elements, too, the ions in compounds are smaller than when free. The atoms of Ca in the pure metal are 3·93 Å. in diameter, and the ions of Ca in lime are 3·42 Å.

Similarly, in organic compounds the ionic sizes are not constant. Aminoff(13) records the measurement of the hydrogen diameter in two hydroxides as 1·15 in one and 1·05 Å. in another.

It has been stated by Davey(2) that the descending arms in Fig. 2 are exactly parallel. There are, however, many exceptions to this rule, and the anticipations based upon it cannot be given much weight.

A more explicit relation of similar type has been given by Scott,⁽¹⁰⁾ and relates to the inter-atomic distance in the crystal lattice. This distance, d, is held to be determined solely by the atomic numbers N_1 and N_2 of two neighbouring atoms, and an empirical relation is suggested:

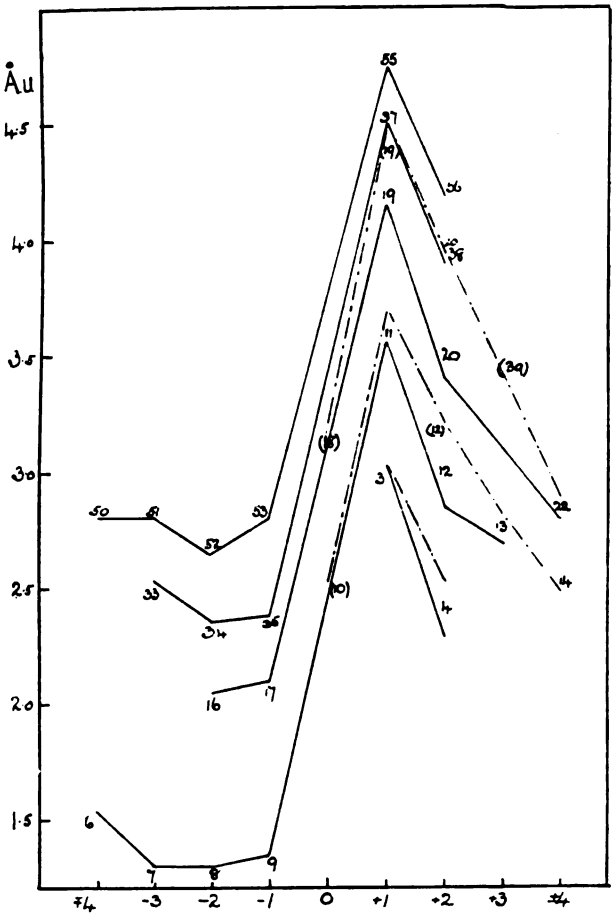


FIG. 2.—" DIAMETERS " OF ATOMS (IONS) IN CRYSTALS, RECORDED BY BRAGG, WITH ATOMIC NUMBERS. DOTTED LINES DUE TO DAVEY.

$$d = a \log (N_1 - N_2) + b.$$

It is, indeed, possible to obtain an approximate logarithmic expression for the shape of the descending parts of the Bragg curve (for the first four elements following each peak), but this cannot be of much significance, and it is impossible to retain the hypothesis of constant atomic " radii " in even its useful approximate form if this formula is accepted.

METHOD 3.—GAS VISCOSITY.

The work of Chapman,(14) Rankine,(15) and others is well known, and has set this method on a very sound footing. It leads directly to the mean area offered by gaseous molecules in elastic collisions between themselves, and the diameters of the molecules can be obtained if their sphericity is assumed, from the formula

$$\pi d^2 = \frac{0{\cdot}347\,\rho V}{N\eta(1+S/T)}$$

This only provides atomic data in the case of the monatomic gas. Rankine(17) has examined the possibility of connecting the diameter of the atom with the size of its molecule. He has also considered the variations in molecular size in series of compound molecules—for example, the effect of the hydrogen protuberance in the successive hydrides of a series is now clear ; but it is not yet possible to estimate the separate atomic sizes.* Some molecular results are recorded in Figs. 3 to 6 ; the only atomic diameters are

He, 1·89 ; Ne, 2·35 ; Ar, 2·87 ; Kr. 3·19 ; Xe, 3·51 (all in Å.U.).

METHOD 4.—EQUATIONS OF STATE.

The value of the co-volume *b* in the Van der Waals equation of state can be obtained for a dozen elements, both from their critical constants and from their behaviour in the gaseous state. Its interpretation rests upon similar hypotheses to those of Method 3, but here the spheres of action are measured, not the mean collision areas, and the reduction from molecular to atomic data is still more uncertain. Chapman's analysis leads to excellent numerical accord in the values of the diameter between the two methods.(19 & 20)

Similar calculations have been based upon the form given to the equation of state by Kamerlingh Onnes, and have led to estimates of atomic diameters by Debye,(21) Keesom,(22) and Zwicky.(23) In their work, however, the atomic fields of force are more explicitly considered, and as these are probably known with less certainty than the atomic dimensions, the results are of less value for our present purpose. Zwicky calculates that the diameter of the helium atom, from the observations at low temperature, is 2·78 Å., and at 20°C. it appears to be 2·25 Å. ; it is more probable that the thermal motion has been inadequately allowed for in the theory than that the equivalent size changes in this proportion.

Results :

(Chapman)	He, 1·96 ; Ar, 2·85 ; Kr, 3·14 ; Xe, 3·42.
(Pease)(24)	Ne, 2.37 ; Ar, 2·93 ; Kr, 3·15 ; Xe, 3·43.

METHOD 5.—COMPRESSIBILITY.

The measurements by Bridgman of the compressibility of the alkali halides have led Richards(25) to some important estimates of atomic size. The pressure volume law for the solid salts is found to contain a " co-volume " term *b*, from which the sizes of the molecules may be deduced. Further, and with more accuracy, the degree to which contraction occurs as the various chlorides are formed is found to be connected in a simple way with the compressibilities of these salts, and the figures permit a clear separation of the contraction in the alkali from that in the halogen. Since the usual atomic volume is well known, the volume of the ion is readily obtained. It increases slightly with the size of the ion with which it is combined—e.g., the caesium ion has an equivalent diameter of 3·66 Å.U. in its chloride, 3·69 Å.U. in the bromide, and 3·82 in the iodide. The halogen ions are constant in volume. The results are for equivalent diameters in Ångstrom units :

---

* Some progress in this direction is recorded by Lorenz,(18) in confirmation of Schroder's law for the addition of atomic volumes, in a considerable number of large molecules.

Cl, 2·8 ; Br, 3·1 ; I, 3·4 ; Li, 2·3-2·6 ; Na, 2·9-3·1 ; K, 3·5-3·7 ;
Rb, 3·8-3·9 ; Cs, 3·7-3·8.

METHOD 6.—VISCOSITY OF LIQUIDS. METHOD 7.—VISCOSITY OF SOLUTIONS. METHOD 8.—DIFFUSION OF IONS. METHOD 9.—MOBILITY OF IONS IN SOLUTIONS.

Jäger(26) extended the ideas of the kinetic theory to the viscosity of liquids, considering the molecules so closely packed that the free path was simply the molecular " diameter." The conditions involved in his analysis are best satisfied by mercury, and for this liquid (and this only) the result is of the right order—$d=3{\cdot}58$ Å.

Measurements of diffusion must lead to dimension data, but at present the only path available to this end is to assume that the diffusing molecule is a sphere, and that it moves against a resistance given by Stokes' law. Einstein's(27) use of this idea for the large molecules of sugar, both in their influence on viscosity in solutions and in their diffusion through organic liquids, is probably sound ; its application for small molecules is very doubtful. Surprisingly good results follow, however, at the hands of Lorenz,(28) who uses Wogau's figures for the diffusion of alkali atoms through mercury. Smith(29) has shown that the ions, and not the atoms, are here being dealt with.

The treatment of the mobility of ions in solution follows a similar path, also first trodden by Lorenz with quantitative success ; but when water is the solvent many special difficulties arise, probably because of the uncertain amounts of hydration. Walden(30) has examined a specially long series of solutions in organic liquids, and applied to them a form of Einstein's result—viz.,

$$d=\frac{15{\cdot}96\times10^{-9}}{u\eta}$$

where u is the velocity of the ion and η the viscosity of the solution. Some of the ionic diameters for solutions in methyl alcohol are :

H, 1·11 ; Cl, 2·49 ; Br, 2·39 ; I, 2·42 ; Li, 4·52 ; Na, 3·48 ; Rb, 2·24 ; Co, 2·22.

These are in descending order of magnitude, and suggest that the smallest ions are most surrounded by attached water molecules. Born's(31) able attempt to carry the theory of the electric forces on molecular dipoles into this domain does not yet lead to probable values for the ionic diameters, although the results are now in the right order :

Li, 0·90 ; Na, 1·02 ; K, 1·34 ; Rb, 1·54 ; Cs, 1·66.

METHOD 10.

An extension(32) of the same ideas to the energy released when a free ion dissolves in water does, however, yield reasonable values. This energy involves the electrostatic field of force of the solvent molecules, and the size of the ion governs the extent to which it enters into this field. It is remarkable that the ionic radius of action as thus specially defined should accord with the usual values. Some results appear in Fig. 3.

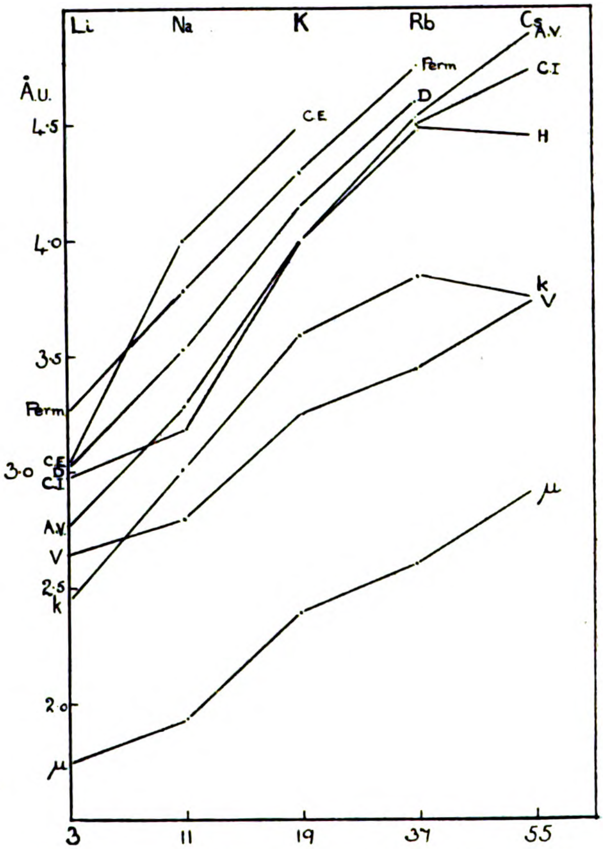


Fig. 3.—Atomic Diameters of Group I Elements.
C.E. : Crystal element (Hull).
C.I. : Crystal ion (Bragg).
Perm. : Permutite (Günther-Schulze).
D. : Diffusion in Hg (Lorenz).
A.V. : Atomic volume—cube root.
H. : Hydratation (Born).(32)
k : Compressibility (Richards).
V : Ionisation potential (Saha).
μ : Molecular refraction (Wasastjerna).

Method 11.

The electrostatic theory of crystal structure due to Born(33) and Landé, and the contributions of Debye(34) towards a more satisfactory electromagnetic theory, lead to values for the ionic radius of action. The former deals with a cubic packing, or, in the form adopted by Bohr,(35) with a tetrahedral unit. Consistent values are only obtained if the positive and negative ions in the molecule are about the same size. Monovalent atoms have been examined by Fajans(36) and Herzfeld, divalent by Grimm,(37) and in these lengthy calculations the repulsion, according to the inverse ninth power law suggested by Born, is supplemented by a repulsion term of the inverse fifth power, representing in greater detail the influence of the charges in the anion upon those of similar size in the kation. The results are diameters varying in the usual way from one member to another within one group, but all of them much smaller than other methods suggest. Grimm's results are :

F, 1·50 ; Cl, 1·90 ; Br, 2·04 ; I, 2·24 ; Ma, 1·04 ; K, 1·58 ; Rb, 1·92 ;
Cs, 2·14 ; Mg, 0·78 ; Ca, 1·34 ; Sr, 1·74 ; Ba, 2·14.

It is clear that here, too, the law of force and the atomic size are inextricably mixed at present, and until further experiments on the variation of compressibility, or of crystal lattice-distances, with temperature, are available this method cannot give reliable information about atomic sizes. It is much better used as a guide to atomic fields of force, and, in particular, may soon lead to an estimate of the relative contributions of the Born and the Debye forces.

METHOD 12.

The study of the scattering of X-rays has led, incidentally, to several estimates of atomic diameters. The best appears to be a result for the diameters of the orbits of the outermost electrons in the sodium and chlorine ions, due to W. L. Bragg(38) and others : Na=1·40, Cl=2·90.

METHOD 13.

Bohr's theory of atomic structure leads directly to the size of the hydrogen atom, and to no other. The diameter of the electron orbit is

$$d=\frac{h^2}{2\pi^2 me^2}=1{\cdot}074\ \text{Å}.$$

The diameter of the positive helium ion should be one quarter of this. Landé's(39) calculations of the rare gas atomic structures and sizes rests on bases now believed to be faulty.

METHOD 14.—IONISATION POTENTIAL.

A simple description of the mechanism of ionisation has been suggested by Eve(40) and by Saha.(41) The detached electron is assumed to move in a circular orbit, and the work required to remove it is inversely proportional to the orbit radius, if the influence of other electrons is neglected. Eve showed that the present meagre data suggest that the factor of proportion varies from group to group among the elements in a regular manner. The figure obtained by the method of Saha for the atomic diameter is a little low for Na, K, etc., lower for Ca, Ba, etc., and much too low for the rare gases, which also suggests that an allowance is required for the other electrons in the outer ring. Some results are shown in the graphs ; others are :

Zu, 1·54 ; Cd, 1·61 ; Hg, 1·39 ; Tl, 1·98 ; Pb, 1·82 ; As, 1·25 ;
Pb, 1·10 ; He, 0·57 ; Ne, 0·90 ; Ar, 1·12.

METHOD 15.

The refractive indices of gases and of aqueous solutions have been examined independently by Heydweiller(42) and by Wasastjerna.(43) The former used Kelvin's idea of the electron displacement within a sphere of positive electricity, and the latter applies a similar idea to the Bohr atom. It is assumed that the electric moment of the molecule is proportional to the volume of the atom; and the estimates of atomic diameters—which are of the right order—refer to an equivalent sphere, as in the Mosotti theory, of electric moment equal to that of the real atom. For dilute solutions the effect is an additive one for the ions concerned, and hence the ionic " diameter " is determined. The results are shown in Figs. 3 to 6. The agreement of these figures with other estimates has been shown indirectly by Calthrop,(44) who has compared the values of $\mu-1$ with the cubes of Bragg's figures, and shown that their ratio is a constant in any one group.

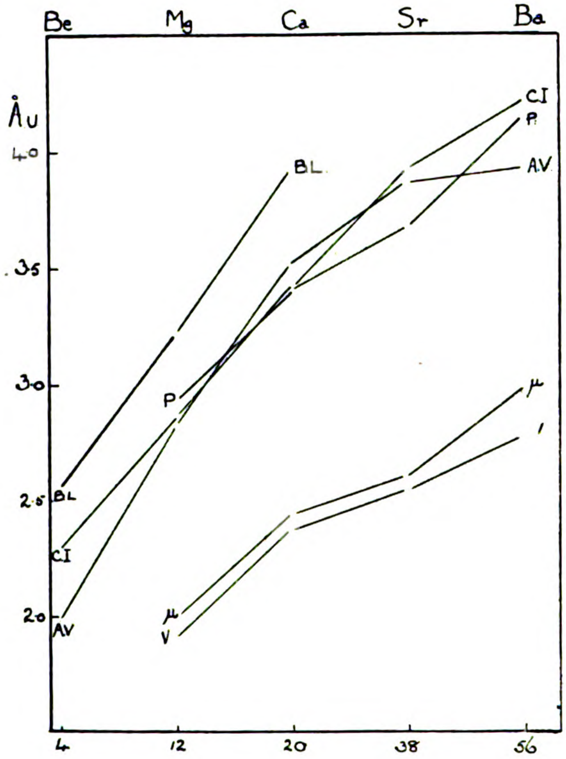


FIG. 4.—ATOMIC DIAMETERS OF GROUP II ELEMENTS.

B-L. : Crystal lattice theory (Born-Landé).
C.I. : Crystal ion (Bragg).
P. : Permutite (Günther-Schulze).
A.V. : Atomic volume—cube root.
μ : Molecular refraction (Heydweiller).
V : Ionisation potential (Saha).

METHODS 15 AND 16.—BAND SPECTRA : CHEMICAL CONSTANT.

Molecular moments of inertia have been very satisfactorily calculated(47) from the infra-red spectra of several gases (H_2, O_2, N_2, H_2O, HCl, etc.), and confirmed by Kratzer's(45) application of a theory of the fine structure of the bands. The same is true of the values deduced by Langen(46) from the values of the chemical constant, based on a statistical sum of molecular energies, though here the experimental results are much less accurate. In both cases the molecular diameter appears to be smaller than is given by other methods.

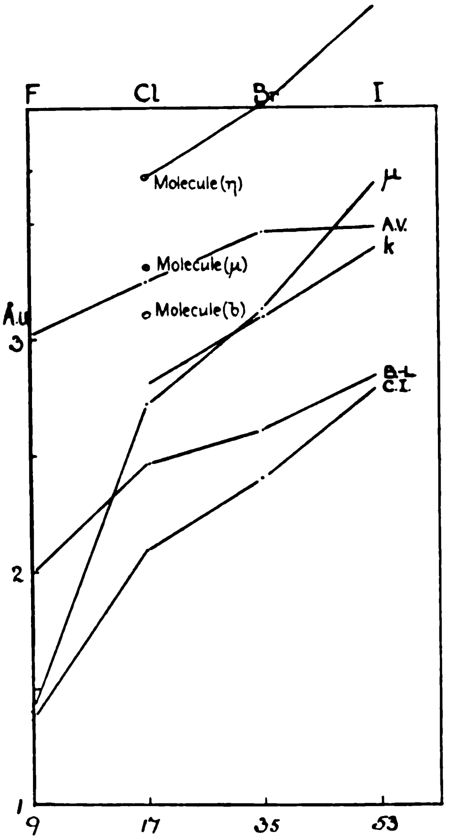


FIG. 5.—ATOMIC DIAMETERS OF GROUP VII ELEMENTS.

μ : Molecular refraction (Heydweiller).
k : Compressibility (Richards).
B.-L. : Crystal lattice theory (Born-Landé).
C.I. : Crystal ion (Bragg).
A.V. : Atomic volume—cube root.

METHOD 17.

It is probable that the amount of optical rotation of a molecule may be connected with the ionic dimensions. It has been pointed out by Brauns(48) that the effect of replacing one halogen by another, in various glucose and xylose compounds, is to alter the molecular rotation by an amount proportional to the difference between the atomic diameters of the two halogens. It is suggested that the dimension of the halogen atoms determines the amount of asymmetry in the molecule, and this determines the rotation. The suggestion has not been further applied.

METHOD 18.—MOLECULAR FILMS.

Many estimates of the dimensions of large organic molecules have been made by the film method, notably by Pockels and Rayleigh in the last century, and by Langmuir,(49) Harkins(50) and Hardy(51) recently. The available methods are at present restricted to these large molecules, and, as comparison with the atomic dimensions is impossible, it is only necessary here to say that they in no way conflict

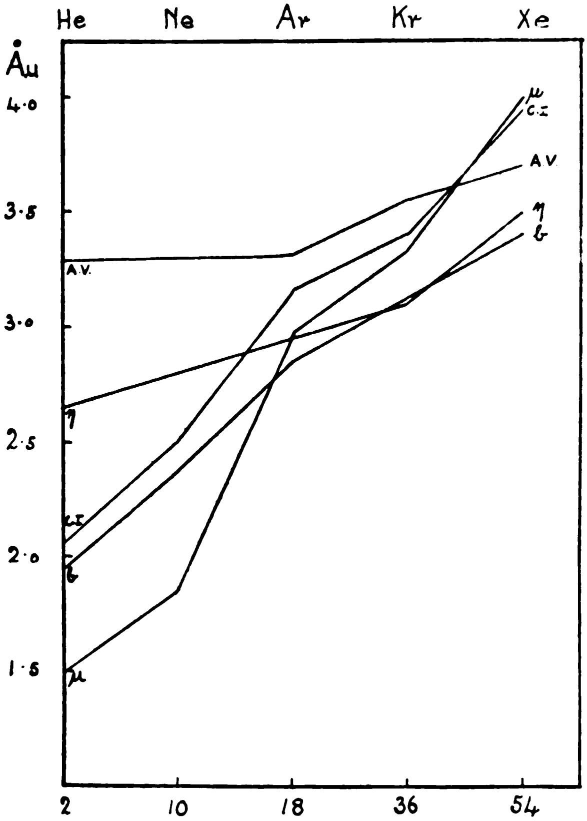


FIG. 6.—ATOMIC DIAMETERS OF RARE GASES.

μ : Refractive index (Wasastjerna).
b : Equations of state (Chapman and others).
C.I. : " Crystal ion " (Davey).
η : Viscosity (Rankine).
A.V. : Atomic volume—cube root.

with the other data. For instance, the dimensions of the molecule of sodium oleate, as carefully estimated from surface tension experiments by du Noüy,(52) are, in three directions, 6·64 Å.U., 7.56 and 12·30 Å.U.

One set of measurements on inorganic substances deserves mention, that by Devaux(53) (repeated by Marcellin).(54) It was shown that unimolecular films of several sulphides and of Ag I could be obtained. For CnS the thickness was 2·7-3·1 Å., which is in good accord with the results of later methods.

METHOD 19.—MAGNETIC THEORIES.

Langevin's theory of diamagnetism leads to a connexion between the susceptibility and the total area of electron orbits within the atom. This latter quantity can therefore be deduced from experimental data, and if the number of circulating electrons is known the diameters of their orbits may be estimated. Pauli(55) (and before him Cabrera) have not found that the results are good, but the deductions made by Young(56) are of the right order for elements. In calculating the contribution of each orbit to the total diamagnetism, Young used the Bohr ratios for the orbital radii, in one case, and replaced the shells of the Langmuir atom by equivalent orbits in a second case ; the results are similar in both cases.

METHOD 20.—ELECTRON STREAM IN A GAS.

The number of electrons which encounter molecules in passing through a gas is a measure of the molecular size.(57) Some gaseous molecules,(58) as O_2 and CO_2, appear to possess a special affinity for electrons which renders the calculation of their size impossible. Further, for the gases chiefly studied, He, Ne, H_2, N_2, the measured size depends upon the speed of the electrons, and reaches a permanent maximum value as this speed falls.(59 & 60) In the case of He and Ne and N_2 this final value is in fair accord with the results from viscosity measurements. For Kr and Xe Ramsauer(61) concludes that the effective atomic cross-section increased from one seventh of the expected value up to five times this value, as the velocities of the electron stream rose from 0·7 volts to 10 volts. Deductions of atomic size are therefore at present impossible.

The bombardment of molecules by a stream of silver atoms has not yet yielded good results on this point, by reason of the great experimental difficulties.

METHOD 21.

Some interesting calculations have been made by Günther-Schulze(63) after measuring the densities of different forms of permutite. In this complex and artificial silicate one ion may be replaced by another in regular order, and the consequent changes in molecular volume are a measure of the differences in the volumes of the substituted ions.

Results :

Li, 3·26 ; Na, 3·78 ; K, 4·30 ; Rb, 4·74 ; Mg, 2·92 ; Ca, 3·38 ;

Sr, 3·66 ; Ba, 4·14 ; Ag, 3·56.

METHOD 22.

Lindemann[64] has suggested that a solid melts when the amplitude of its heat vibrations is such that neighbouring atoms collide, and this leads to good results for many metals.

CONCLUSION.

The chief numerical results are collected and shown in Figs. 3 to 6. The accord between the different methods is, on the whole, very promising. Finally, in Fig. 7, a rough mean has been taken from the preceding figures, and the variation in size throughout the groups is presented in a way which shows both the increase in size as the number of electron " rings " or " shells " is increased, and also the contraction which goes on as the number of electrons in the outer ring is increased. The figures

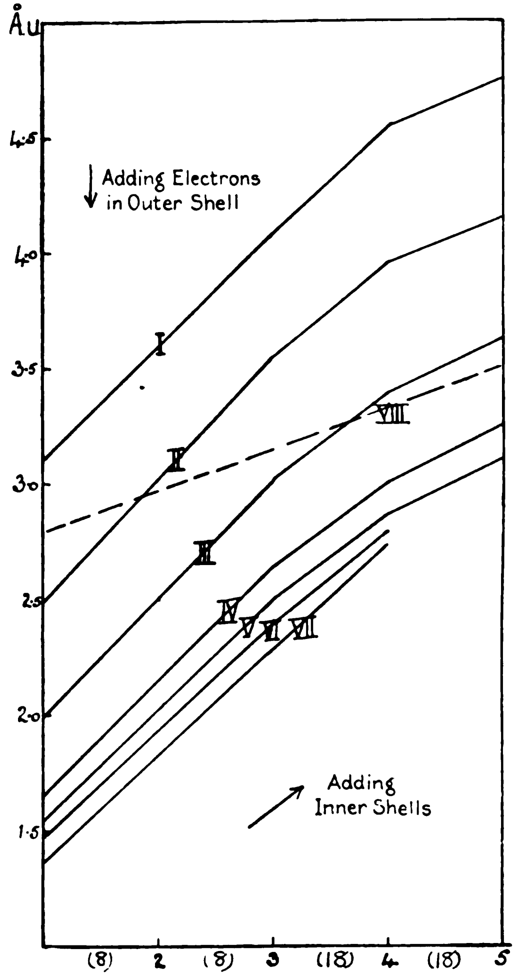


FIG. 7.—MEAN " ATOMIC DIAMETERS " FOR ELEMENTS OF ALL GROUPS.

for the electronegative elements rest necessarily too much upon two methods only; and they do not settle the most interesting question—whether the contraction continues up to the seventh group, as shown, or whether the increase which is striking in the 8th group really commences with the 7th or the 6th. There is evidently a parallelism among the groups; and the effect of adding an inner shell is an increase in diameter of, roughly, 0·5 Å. in every case.

REFERENCES.

(0) Herzfeld, Jahrbuch d. Rad. u. Elektronik, 19, p. 259 (1922).
(1) W. H. and W. L. Bragg, "X-rays and Crystal Structure," pp. 160-180, 4th edn. (1924).
(2) Davey, Phys. Rev., 23, p. 318 (1924).
(3) Biltz, Zeits. Anorg. Chem. (1923).
(4) Pierrucci, Nuovo Cim., 19, p. 109 (1920).
(5) Herz, Z. Anorg. Chem., 105, p. 171 (1919).
(6) Quoted by Sommerfeld, " Atomic Structure," p. 99 (1923).
(7) Lorenz, Z. Anorg. Chem., 111, p. 147 (1920), and earlier Papers.
(8) Wyckoff, Proc. Nat. Academy, 9, p. 34 (1923).
(9) Davey, Phys. Rev., 22, p. 29 (1923).
(10) Scott, J. Phys. Chem., 29, p. 306 (1925).
(11) W. L. Bragg, Phil. Mag., 40, p. 169 (1920).
(12) Havighurst, J. Amer. C. S., 46, p. 2368 (1924).
(13) Aminoff, Chem. Abs., 126, 652 (1924).
(14) Chapman, Phil. Trans. A., 216, p. 279 (1915).
(15) Rankine, Proc. Roy. Soc., 99, p. 331 (1921), and earlier Papers.
(16) *e.g.*, Kia Lok Yen, Phil. Mag., 38, p. 582 (1919); Günther-Schulze, Zeits. f. Ph., 11, p. 260 (1922).
(17) Rankine, Proc. Faraday Soc., 17, p. 719 (1922)
(18) Lorenz, Z. Anorg. Chem., 111, p. 48 (1920).
(19) Millikan, Phil. Mag., 34, p. 1.
(20) Rankine, Proc. Roy. Soc., 98, p. 360 (1921).
(21) Debye, Phys. Zeits., 22, p. 302 (1921).
(22) Keesom, Phys. Zeits., 22, p. 643 (1921).
(23) Zwicky, Phys. Zeits., 22, p. 449 (1921).
(24) Pease, J. Amer. Chem. Soc., 44, p. 769 (1922).
(25) Richards, Proc. Amer. Chem. Soc., p. 422 (1923).
(26) Jäger, Wien Ber., 108, p. 54 (1899).
(27) Einstein, Ann. d. Phys., 19, p. 289 (1906).
(28) Lorenz, Zeits. f. Ph., 2, p. 175 (1920).
(29) Smith, Zeits. f. anorg. Chem., 88, p. 161 (1914).
(30) Walden, Zeits. f. anorg. Chem., 113, p. 125 (1920).
(31) Born, Zeits. f. Ph., 1, p. 221 (1920).
(32) Born, Zeits. f. Ph., 1, p. 45 (1920).
(33) Born, Verh. d. D. Phys. Ges., 21, p. 13 (1919), and earlier Papers.
(34) Debye, Phys. Zeits., 22, p. 302 (1921).
(35) Bohr, Zeits f. Phys., 9, p. 1 (1922).
(36) Fajans and Herzfeld, Zeits. f. Phys., 2, p. 309 (1920).

(37) Grimm, Zeits. f. Ph. Ch., 98, p. 353 (1921).
(38) Bragg, James and Bosanquet, Phil. Mag., 44, p. 433 (1922), and earlier Papers.
(39) Landé, Phys. Zeits., 21, p. 626 (1920).
(40) Eve, Nature, 107, p. 552 (1921).
(41) Saha, Nature, 107, p. 682 (1921).
(42) Heydweiller, Ann. d. Phys., 49, p. 653 (1916).
(43) Wasastjerna, Zeits. f. Ph. Ch., 101, p. 193 (1922).
(44) Calthrop, Phil. Mag., 47, p. 772 (1924).
(45) Kratzer, Ann. der Phys., 67, p. 127 (1922).
(46) Langen, Zeits. f. El., 25, p. 25 (1919).
(47) Imes, Astrophysical Jour, 50, p. 251 (1919).
(48) Brauns, J. A. C. S., 47, p. 1285 (1925), and earlier Papers.
(49) Langmuir, J. A. C. S., 39, p. 1848 (1917).
(50) Harkins, J. A. C. S., 44, p. 653 (1922).
(51) Hardy, Proc. Roy. Soc., 100, p. 550 (1921).
(52) du Noüy, Phil. Mag., 48, p. 664 (1924).
(53) Devaux, Journ. de Phys., 3, p. 450 (1904).
(54) Marcellin, Ann. der Phys., 1, p. 19 (1914).
(55) Pauli, Zeits. f. Phys., 2, p. 201 (1920).
(56) Young, Trans. Roy. Soc. Canada, 16, p. 49 (1922).
(57) Lenard, Ann. d. Phys., 12, p. 449 (1903).
(58) Franck and Hertz, Phys. Zeits., 20, p. 132 (1919).
(59) Townsend, Phil. Mag., 44, p. 1033 (1922).
(60) Mayer, Ann. d. Phys., 64, p. 451 (1921).
(61) Ramsauer, Ann. d. Phys., 66, p. 546 (1921).
(62) Born, Phys. Zeits., 21, p. 578 (1920).
(63) Gunther-Schulze, Zeits. f. Ph., 5, p. 324 (1921).
(64) Lindemann, Phys. Zeits., 11, p. 609 (1910).

DISCUSSION.

Prof. A. M. TYNDALL : The Paper is a very useful summary of experimental data. At the same time it would be more valuable if an account of the recent important theoretical work of Lennard-Jones could be incorporated in it. On modern theories one must emphasize the difference between atomic and ionic sizes. For instance, the position of sodium in a table of the dimensions of the various elements is different according to whether one is thinking of the uncharged atom or of the positive ion. The atomic volume results refer to the former, and Wasastjerna's to the latter. Consequently, therefore, the " average " values given in Fig. 7 can hardly be regarded as having a real physical significance.

Dr. J. H. VINCENT said that in Fig. 1 the straight line representing the rare earth elements is marked with a reference to the element 72, which thus occurs twice. It would be better to substitute " 71 " in this figure. The graph could be more conveniently drawn to logarithmic scales ; this plan would facilitate certain adjustments in the case of the ordinates, and in the case of the abscissæ (valencies) it would obviate the necessity for an arbitrary change of scale for the long periods. The negative valencies could be represented by the logarithms of the valency numbers plotted leftwards from the origin.

Mr. J. E. CALTHROP : In such an extensive list of references, I think some mention might be made of a Paper on "Molecular Diameters," by H. Sirk (Phil. Mag., 49, pp. 708-711, 1925). The diameters for a number of substances are calculated from latent heats of vaporisation, and the values obtained appear to be about 1·37 times the corresponding values derived from the Kinetic theory of gases. The result for Argon is a diameter of 3·6A. in good agreement with 3·8A. found from X-ray measurements on crystal Argon by Simon and Cl. v. Simson. Both these values are greater than the value given in Fig. 7 of Mr. Lunnon's Paper.

Prof. T. H. LABY said that, since modern views of atomic structure preclude us from regarding the atom as an elastic sphere, the diameter measured by each method is really a different quantity; the differences between the results obtained represent real physical differences, and not experimental errors. X-ray measurements are accurate to 0·1 per cent., and even observations on gas molecules give an error less than the differences between the results obtained by different methods. It is, therefore, incorrect to take a mean value of all the results.

Dr. GEOFFREY MARTIN: This Paper appeals to chemists as well as to physicists. In fact, many of the Papers read before the Society are of considerable chemical interest, and I think it rather a pity that the dates of many chemical functions overlap those of physical meetings, and make it a difficult matter for anyone to attend both series of meetings, especially as I think that chemists and physicists should co-operate together more than they do. Recently I have been carrying out researches on the fine grinding of quartz sand. I have measured the weights, diameters and surfaces of both very coarse and very fine particles, and have proved that they possess the same average shape. One curious practical application of molecular dimensions is that they can be utilised for determining the mechanical efficiency of grinding machinery in absolute terms. One imagines the power to be reduced to molecular dimensions. Then the work theoretically required to do this is the total heat of volatilization. By assuming a straight line law and measuring the power absorbed in the actual grinding operations, I have shown that the efficiency of the tube mill is only about 1/15th per cent.

When reading the Paper I was reminded of work that I carried out as a young man over 20 years ago. The periodic table of Mendeleef was used as a base, and from each element an ordinate was erected proportional to the chemical attraction it possessed for any one atomic species (as measured by the heat of formation or decomposition of its chemical compounds with that atomic species). In that way a series of surfaces was obtained, one peculiar to and characteristic ot each elementary substance. It was proved that chemically similar elements produced similarly shaped surfaces, and therefore two elements were chemically similar when they exerted, not equal, but *proportional* forces on the same elementary atoms. Also that when any element (say iron) entered a different valency state it produced a different surface. So that when an element changed its chemical forces it changed its chemical characteristics. Consequently the properties, both chemical and physical, of an element were decided entirely by the forces it exerted. Two elements would possess the same properties and could replace each other (no matter what their atomic weights were) if they exerted the same forces.

Dr. P. E. SHAW (communicated): In Papers before the Physical Society (1900) and Royal Society (1905) I showed the possibility of setting two surfaces at the small distance apart of $0{\cdot}5 \times 10^{-7}$ mm. These distances, which were measured by the electric micrometer and telephone, are little, if any, more than the atomic dimensions of the metals of which the surfaces are made. I have not been able to follow up the curious effects audible in the telephone when the electric discharge occurred between the surfaces, which had been maintained as some very small P.D. The sounds heard were peculiar for certain metals, notably lead. It seems to me that some use might be made in present-day sub-atomic research of this method of obtaining a very small gap or slit.

AUTHOR'S reply: It is clear that a different atomic dimension is measured by each of the methods referred to in this Paper, and that it would be wrong in principle to claim any absolute significance for the lines of Fig. 7. Nevertheless the surprising similarity between the result of different theories makes it very probable that the diagram is on sound lines in its suggestions as to the variation of size from atom to atom within each group, and from group to group; and its only purpose is to show the trend of these variations. The Paper affords evidence that the variations are similar whether ions or neutral atoms are considered. A discussion of the exact meaning of " diameter " was purposely excluded from this brief survey, and for this reference must be made, for example, to the Papers of Lennard-Jones (Proc. Roy. Soc., 109, 476, 1925, and previous Papers).

XIV.—ON EDGE-TONES (I).

By W. E. BENTON, *B.Sc.*, University of Birmingham.

(*Communicated by* PROF. S. W. J. SMITH, *F.R.S.*)

ABSTRACT.

An edge-tone is heard when a stream of air issuing from a slit or hole strikes a sharp edge, or surface bounded by sharp edges. A brief description is given of previous work, and it is shown that the eddies which give rise to edge-tones conform to a simple Kármán vortex-system. On the assumptions (1) that the distance a from the edge to the slit is always equal to l, the distance between two eddies in the same row, and (2) that tone is destroyed when the edge—when moved across the jet towards still air—crosses the line of eddy centres, one can measure h/l, where h is the separation of the eddy-rows, directly from measurements of the boundaries for tone. From the experiments it is found that at low pressures and with wide slits h/l, for air, $=0{\cdot}276$, which may be compared with v. Kármán's prediction of 0·283 for an infinite system in a perfect fluid.

If the edge is moved towards the slit, h, the separation of the eddy-rows, must decrease proportionally. The experiments show that when the eddies are formed very close to the edges of the slit, and therefore in a field of high velocity-gradient at right angles to the direction of motion, they are deflected towards the middle, or principal, plane of the jet. The amount of this deflection increases very rapidly as a approaches a_0, at which distance tone can only be obtained when the edge lies in the principal plane. The experiments show that with wide slits, when $a=a_0$, then $l=a_0$; $h=0{\cdot}67d$, where d is the width of the slit. The minimum distance for tone, a_0, varies with the velocity v, and the width of the slit.

The results suggest an equation of dynamic similarity :—

$$B\left(\frac{\nu}{vd}\right)=\left(\frac{a_0}{d}\right)^2-1{\cdot}50$$

where B is a number (about 2,000 for air) and ν is the coefficient of kinematic viscosity. By considering the acceleration that produces the deflection, an expression of somewhat similar form can be obtained theoretically. The tonal boundaries in the region of simple tone approach two straight-line asymptotes, equally inclined to the principal plane, which converge at a point 0 near the plane of the slit. If $\bar{a}$ and $\bar{a}_0$ denote the distance of the edge and the minimum distance for tone respectively from 0, the total separation, y, of the two boundaries at any distance $\bar{a}$ is given by the equation :—

$$y=\frac{h}{l}\bar{a}-\frac{h}{l}\bar{a}_0e^{-m^2(\bar{a}^2-\bar{a}_0^2)}$$

where $1/m$ is approximately equal to d, when the slit is very wide. The measurements of the frequency of the tone and the deductions made from them will form the subject of a subsequent communication.

A. INTRODUCTION.

THE natural frequency of vibration of a body of air contained in a pipe or resonator may be excited by blowing gently across the aperture—in the case of a pipe, across the open end. It was formerly believed that the action of the air-jet was similar to that of a clock-escapement, the motion depending essentially on the assistance of the air contained within the resonator. Recently it has been established that the origin and maintenance of the tone of a flue organ-pipe are due to the natural vibration, about the rigid upper lip, of the thin stream of air issuing from the throat (Kernspalt). The investigation of this natural motion, when remote from the influence of a resonator, comprises the study of edge-tones. The general characteristics of edge-tones were first described by Sondhauss, and his results have been repeated and extended by Hensen. Weerth, Wachsmuth and Kreis. They noted that the edge must be parallel to the plane and to the direction of length of the slit, and should be in the middle of the air-stream, in what we may call the principal plane of the jet.

When the edge is very close to the slit, no tone is obtained. At a distance a_0 (dependent on the nature of the gas, the width of the slit and on the velocity of the jet) a note suddenly appears, of a pitch dependent principally upon the velocity and the value of a_0. As the distance is increased the pitch of the note falls steadily until at a distance a_1 the note suddenly "jumps" to its octave. As the distance is still further increased the frequency again falls, until at a distance a_2 it jumps suddenly to the "fifth" above. Subsequently, at a_3, there occurs a jump of one-fourth, and under certain conditions six or eight of these breaks may be detected. In 1912, W. König, using Göller's experimental work at Rostock, suggested that the frequency n of an edge-tone is given by the formula

$$n=\frac{vi}{2a}$$

where v is the total quantity of air per second, leaving each sq. cm. of the slit; a is the distance of the edge from the slit, and

from	a_0 to a_1	$i=1$
	a_1 to a_2	$i=2$
	a_2 to a_3	$i=3$, etc.

König tentatively suggested that

$$a_0=\frac{a_1}{2}=\frac{a_2}{3}=\frac{a_3}{4}, \text{ etc.}$$

The difficulty of measuring air-velocities led Schmidtke to prefer the use of a jet of water, issuing into water, and his observations show that König's formula is approximately true for water.

B. Apparatus.

In commencing the present work, it was decided to preserve the following conditions :—

(1) The air-jet to issue from a region of still air.

(2) The jet to leave the slit perfectly smoothly.

(3) The jet to be normal to the plane of the slit.

(4) To avoid possible distortion of the streamlines by allowing the presence of no large object near the jet.

(5) The edge to be rigid and sharp.

(6) The approach to the slit, from inside, to be streamlined, so that the jet undergoes no contraction after leaving the slit.

(7) The air-pressure and the slit-width to be adjustable.

(8) The edge to be able to move in directions parallel and perpendicular to the central (or principal) plane of the jet.

The apparatus shown in Fig. 1 adequately fulfils these conditions. Compressed air is admitted through the tap A into the wind-chest B. The turbulence produced at the top is destroyed by passing the air through a sheet of fine wire gauze at C.

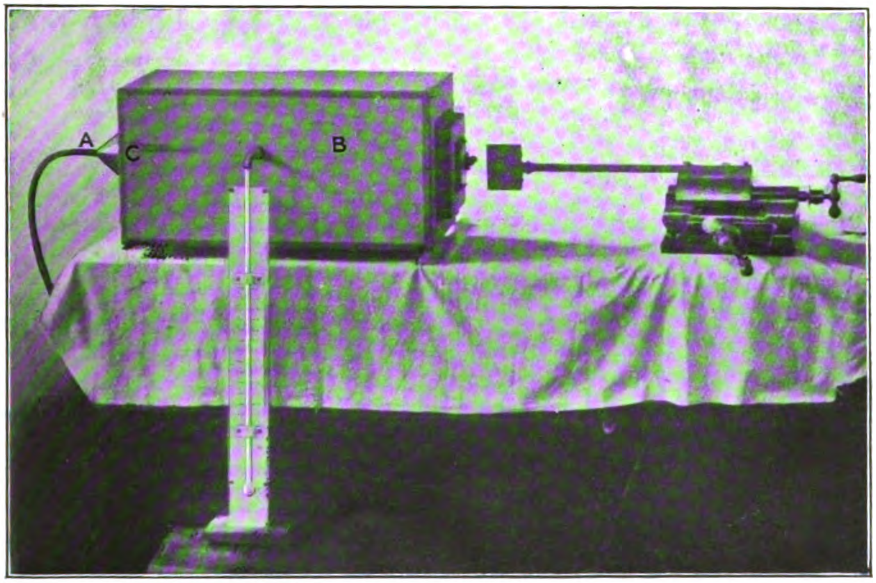


FIG. 1.

To face page 110]

UNIV. OF MICH.

To prevent the formation of any central stream of rapidly moving air, the centre of the sheet is blocked out with solder. The cross-section of the box (900 sq. cm.) is so great compared with that of the slit—seldom more than 1 sq. cm.—that the air in the box may be considered at rest. The vertical water manometer, introduced mid-way in the length of the box, may therefore be considered to read the actual excess pressure to which the velocity of the jet is due. The corners of the box on the forward face are covered inside by a metal cone which prevents the formation of any " dead-space " in which large eddies might easily arise. All other edges are similarly removed, so that the air approaches the slit, formed between two polished brass edges, in easy streamline motion. The inner edges of the slit are bevelled, so that eventually the air leaves normally to the plane of the slit. The length of the slit is 10 cm.* The edge to be introduced into the air-stream is of mild steel, bounded by two polished plane faces enclosing an angle of about 5°, mounted at the end of a long iron bar (1 ft. in length by ½ in. square), fixed rigidly to the movement carriage. It was considered necessary to remove so large a mass as that of the movement carriage from the vicinity of the jet, and the bar supporting the edge, though long, was strong enough to resist vibration. The movement carriage, which was firmly fixed to the table, enabled the edge to be moved in directions perpendicular and parallel to the principal plane of the jet, with an accuracy of movement of about 0·001 cm. in either direction over distances of about 1 cm. Very small distances, such as those occurring in the tonal-boundary measurements, could be estimated to 0·00025 cm. The total possible movement was some 20 cm. perpendicular to, and 10 cm. parallel to, the principal plane of the jet.

This process of removing all sources of complication and error, however, also removed the most interesting characteristic of the edge-tones studied by Wachsmuth, namely, the succession of breaks in the tone as the distance of the edge from the slit increases. Using a narrow slit, and moving along the principal plane, a bright clear tone appears at a distance $a=a_0$. This undergoes small variations in quality as the distance increases, the bright octave quality changing gradually to an almost pure tone, and thence to an unpleasant nasal sound. The nasality increases rapidly as a approaches a value a_1, when a harsh discordance suddenly appears. Here the former tone can be recovered, somewhat thinner in quality, by moving the edge slightly across the jet. In the present experiments measurements have been confined to the simple region of comparatively pure tone.

C. THEORY.

Wachsmuth's " Schlierenbilder " show that in the first interval ($a_0<a<a_1$) an eddy on the left-hand side of the jet is about to pass the edge when another on the same side is being formed at the slit, while on the right-hand side a third eddy lies half-way between the slit and the edge. The period of oscillation is the interval of time between the release of two successive eddies on the same side of the jet—i.e., for this particular state the period is the time taken for the eddy to move from the slit to the edge. Now, if the eddies were very small, and if the air-stream could be considered as a sharply-defined belt of moving air, one might assume that an eddy moved as a " roller " in contact with a moving belt, having at any instant a point in contact with the belt moving with velocity v, and one point furthest from the

---

* Wachsmuth used a slit 1 cm. long. Hensen's slit was 4 cm. long.

belt, momentarily at rest. The velocity of the eddy would then be one-half the velocity of the belt, and the time taken to traverse the distance a would be $2a/v$. The frequency of vibration of the air-stream about the edge would therefore be given by

$$n=\frac{v}{2a}$$

which is König's formula.

A wind-tone of any kind is the acoustical result of the formation of two parallel rows of eddies (or of eddy-rings lying on two coaxial cylinders) advancing with uniform velocity.

Th. von Kármán considered the perfect case of two infinite parallel rows of rectilinear vortices in which the senses of rotation of eddies of the same row are like, of different rows unlike. He showed that there is only one possible arrangement for such a system in a perfect fluid to move forward unchanged. The eddies of one row must be placed alternately with respect to those of the other, and the ratio of h, the distance between the two rows, to l, the distance between two adjacent eddies in the same row, must satisfy the equation

$$\cosh\left(\frac{h}{l}\pi\right)=\sqrt{2},$$

i.e.,
$$\frac{h}{l}=0{\cdot}283\ .\ .\ .\ .$$

v. Kármán and Rubach made a few experiments with water models and found from photographs 0·305 and 0·280 for values of $\frac{h}{l}$.

The system of eddies that gives rise to edge-tones differs from this ideal case in two ways, for it is supported against frictional destruction by a central belt of high velocity, and the edge in some way is absolutely necessary to the formation of the eddies. Instead of two parallel rows of eddies infinite in both directions, one has a system infinite in one direction only, with a rigid barrier placed between the rows extending to within the distance l of the source. This interval between the slit and the edge may be termed the free space of the system. At any moment each of the three eddies existing in the free space must move with a resultant velocity due to the other two eddies, and the deformation of the system which would inevitably result in time from this motion is checked by the intervention of the edge which separates the members of one row from those of the other, and forces them to continue a uniform progress. The action of the edge-wall on an eddy after passing the edge is such that the normal component of velocity at the wall is zero. If a new eddy were introduced of equal strength, but of opposite sense of rotation, in the position of the optical image of the first eddy with respect to the wall, one could remove the wall without affecting the motion of the fluid. Hence we could hypothetically do away with the edge, if we introduced one of these images for every eddy that had passed the edge. The total effect of such a substitution would be two eddy systems superimposed on the same parallels, and both infinite in one direction only, one system, however, being laterally inverted with respect to the other, and having its origin displaced by the system-interval l in the direction of motion.

That such a system has some peculiar stability of its own is evidenced by its occurrence in experiment in the working of that useful little instrument the bird-call (Vogelruf, Jageruf), and also in the formation of the tones produced by the passage of air through tubes of pressed metal strip, recently observed by Cermak.

In the bird-call a stream of air passes successively through two circular holes in thin parallel metal plates. The second hole traversed by the air should be slightly larger than the first, and its centre must lie on a line drawn perpendicular to the plane and through the centre of the first hole—i.e., on the axis of the system. The first hole alone would tend to produce an unstable system of eddy-rings, the axes of rotation of the rings lying on two cylinders of diameters slightly greater and slightly less than the diameter of the first hole.* The second hole produces a similar system of eddy-rings with their axes on the same cylinders, and the combined formation is stable when the origin of the second system is displaced a distance l from that of the first, the two systems being laterally inverted with respect to each other. In most bird-calls the space between the plates is enclosed, producing a natural resonator, which exerts an action upon the wind-tone similar to that of an organ-pipe upon the edge-tones produced at the mouth.

D. MEASUREMENT OF $\frac{h}{l}$.

In order to measure $\frac{h}{l}$, v. Kármán and Rubach photographed the eddies produced in a current of water behind a stationary plate, and conversely behind a moving plate in still water. In air, both the frequency of production and the velocity of translation of the eddies are usually very high, and Wachsmuth's photographs show that even when the air-jet (loaded with ether-vapour to render it refrangible) is photographed, the eddies do not clearly appear, since they are largely formed of entrained air, which does not differ optically from the surrounding medium. From a consideration of the nature of the eddy-system, a very simple method of measuring $\frac{h}{l}$ was devised. Wachsmuth and Hensen both noticed that when the edge was moved across the air-streams changes occurred in the frequency of the tone, and also a boundary was reached at which all tone vanished. With the present apparatus the lateral boundaries are very sharply defined. With a narrow slit a position can be found from which a lateral movement of 0·0005 cm. will completely extinguish a clear bright tone. The least turbulence in the jet spoils this definition completely. v. Kármán's work readily suggests an explanation.

Consider the edge at some distance a from the slit (Fig. 2). Then for stability we may assume that the eddy-centres move on two lines AB, CD, each distant $\frac{1}{2}\frac{h}{l} \cdot a$ from the principal plane. If the edge is moved across the stream towards AB, a point will be reached when an eddy on that line will be caught by the edge and deflected to the side CD. The tone cannot then exist. Assume for simplicity that this point is on the path traversed by the eddy-centre. When the edge reaches either AB or CD, the tone will be destroyed. If a is changed, the total lateral movement (*AB* to *CD*), which may be denoted by *y*, will be changed in the same proportion.

---

* This system can be rendered stable by employing a sharply cut hole in a thick plate (Kohlrausch).

$$\frac{\delta y}{\delta a}=\frac{h}{l}=\text{const.}$$

Fig. 3 is a typical map of a tonal boundary. The sudden change of slope observable in both maps occurs at the discordant break. Increase of pressure moves the whole diagram towards the slit. At high pressures it is difficult to obtain consistent readings of the boundaries. The break moves forward very rapidly as the pressure increases, until the interval $a_0<a<a_1$ is very small indeed. A very small change of pressure during the course of the experiment will entirely spoil the readings. All the maps show a rounded-off portion at a_0, which we may call the "nose" of the diagram. This we will consider presently.

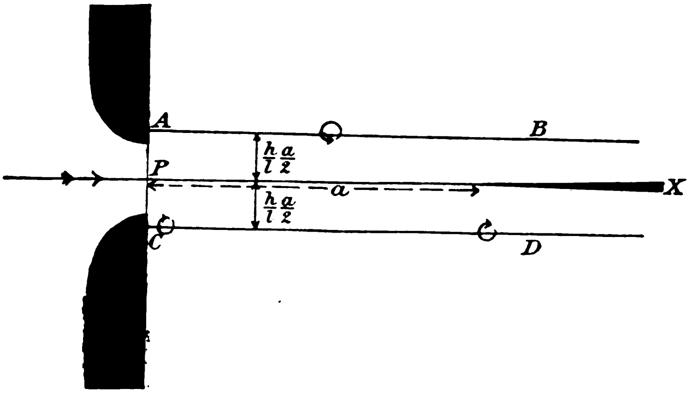


FIG. 2.

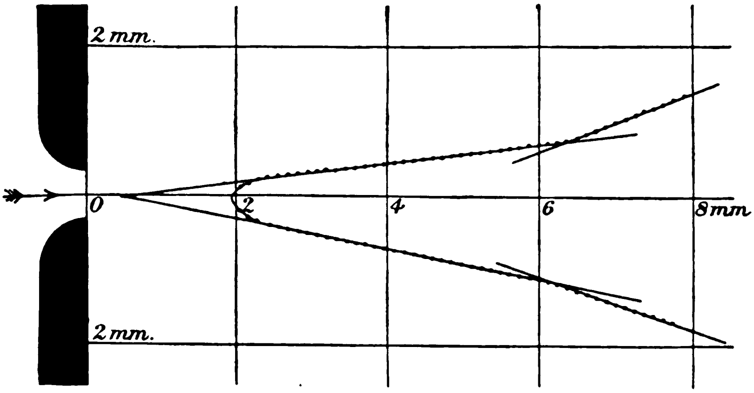


FIG. 3.

In Table I are given the measurements of $\frac{h}{l}$ from the tonal boundaries for different pressures and slit-widths. An increase of pressure appears to increase $\frac{h}{l}$ slightly, a minimum value characteristic of the slit-width being attained at low pressure. For very wide slits $\frac{h}{l}$ for air attains a minimum value of 0·276 independent of the slit-width. It may be questioned whether these numbers are really values of $\frac{h}{l}$. The reasoning was based on the assumptions that (1) $a=l$, (2) that the point of disappearance of the tone occurs when the edge reaches the line of eddy-centres. The diagrams themselves show that one must substitute a linear relation

$$a=l+\varphi(p,d)$$

where φ is some function for the simpler equation

$$a=l$$

The second assumption has no experimental support.

TABLE I.

d	Pressure in cm. of water	$\frac{h}{l}$
0·010 cm.	1·01	0·50
	1·98	0·515
0·0365 cm.	0·10	0·32
	0·19	0·33
	0·68	0·35
0·077 cm.	0·34	0·32
	0·62	0·32
0·104 cm.	0·38	0·30
	0·63	0·31
0·132 cm.	0·25	0·285
	0·45	0·309
0·148 cm.	0·25	0·276
	0·39	0·287
0·188 cm.	0·21	0·276

E. DETERMINATION OF a_0.

In Fig. 9 *PC* represents the minimum distance for tone, a_0. *O* may be called the origin and *P* the pole of the system An increase of pressure diminishes *PC*. Fig. 4 represents the change of a_0 with pressure for different slit-widths. These curves are not hyperbolæ. In each experiment it was found that a small minimum pressure p_0 existed, below which no tone however faint could be obtained.* As the pressure approaches p_0, a_0 increases very rapidly, and the tones become so faint and so low in pitch that the values of a_0 are difficult to obtain. p_0 is usually about 0·2 cm. of water, and apparently depends on the slit-width, and possibly on the weather conditions. It may represent a small difference of humidity between the interior and exterior of the wind-chest.* Fig. 5 shows the relation between $\frac{1}{\sqrt{p-p_0}}$ and a_0. Each curve when produced cuts the axis $a_0=0$ at some value $\frac{1}{\sqrt{p-p_0}}=-f$ and the axis $\frac{1}{\sqrt{p-p_0}}=0$, at some value $a_0=A$.

---

* Sondhauss said in 1854 : " Below a certain pressure, no tone could be heard."

Fig. 6 shows the relation between

$$\sqrt{\frac{1}{\sqrt{p-p_0}}+f} \text{ and } a_0.$$

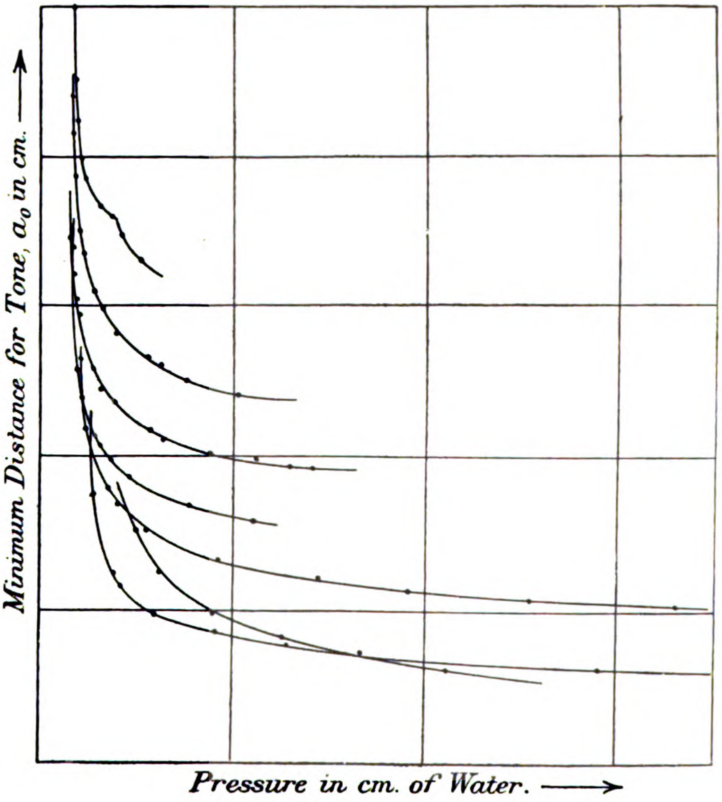


FIG. 4.

Air leaving a slit without resistance under simple adiabatic expansion from a pressure P_1 to a pressure P_0 should attain a velocity $\bar{v}$ given by

$$\bar{v}^2=\frac{2\gamma}{\gamma-1} \cdot \frac{P_1}{\rho_1}\left\{1-\left(\frac{P_0}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right\}$$

where γ is the ratio of the specific heats $\frac{C_p}{C_v}$, and ρ_1 is the initial value of the density.

---

* $p_0{}^2d$ is approximately constant, where d is the width of the slit.

For the present purposes, where P_1 is only very slightly greater than P_0 $\left(\frac{P_1}{P_0} \simeq 1{\cdot}001\right)$ the equation may be simplified. If the manometer records a difference in level H of liquid of density ρ_m, we have

$$P_1 = P_0 + \rho_m g H$$

and

$$\bar{v}^2 \simeq 2 \frac{\rho_m}{\rho_0} gH$$

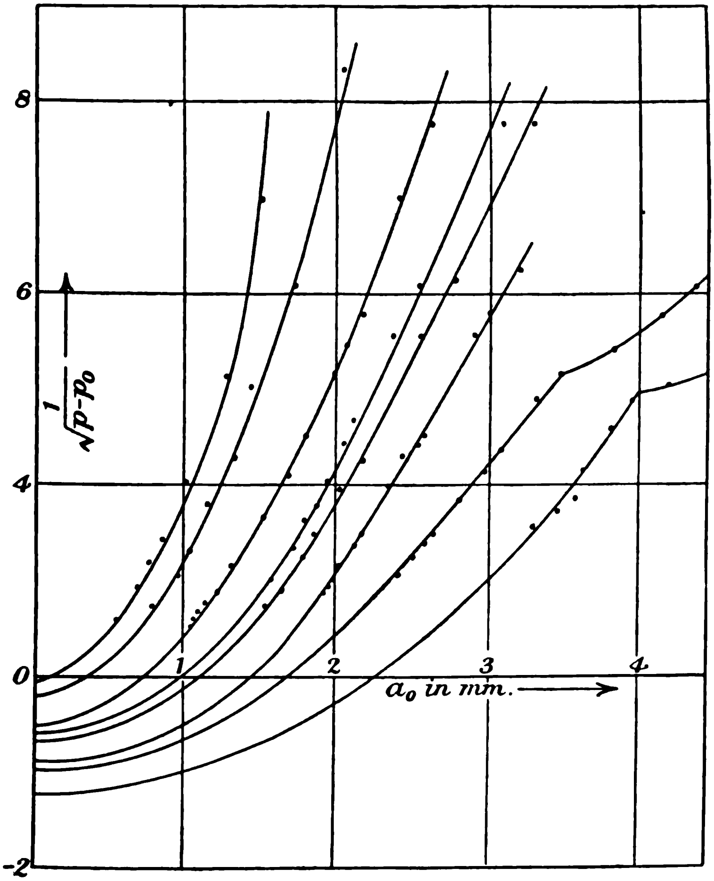


Fig. 5.

For a water manometer at 0°C. and air initially at the same temperature, we have numerically in c.g.s. units

$$\bar{v} \simeq 1232 \sqrt{H}$$

In these experiments the air left a slit formed between polished brass surfaces, the approach to which was stream-lined, and under such conditions it was hoped that there could be no great error in the assumption

$$\sqrt{p - p_0} = v,$$

where v is a quantity proportional to $\bar{v}$.

The quantity f appears to have no direct physical significance. The length A, however, when plotted against the slit-width d, gave a straight line passing through

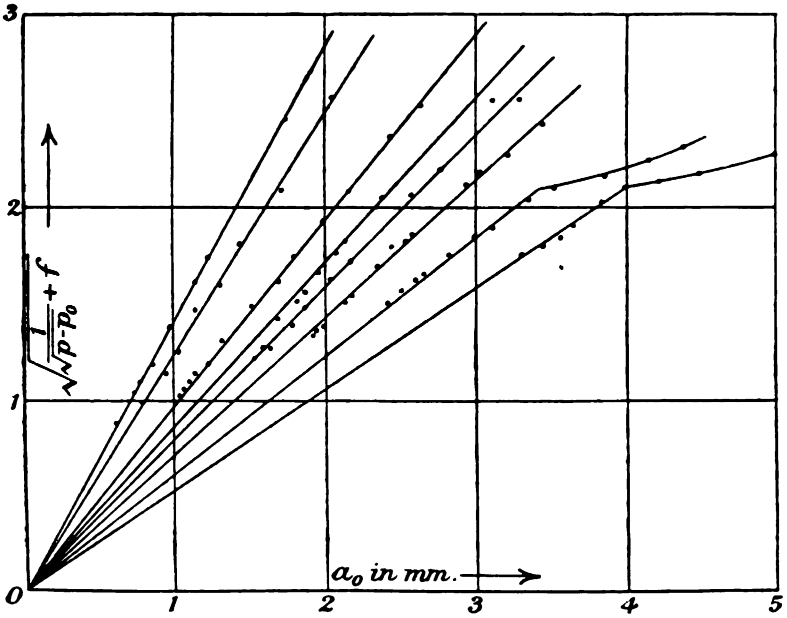


FIG. 6.

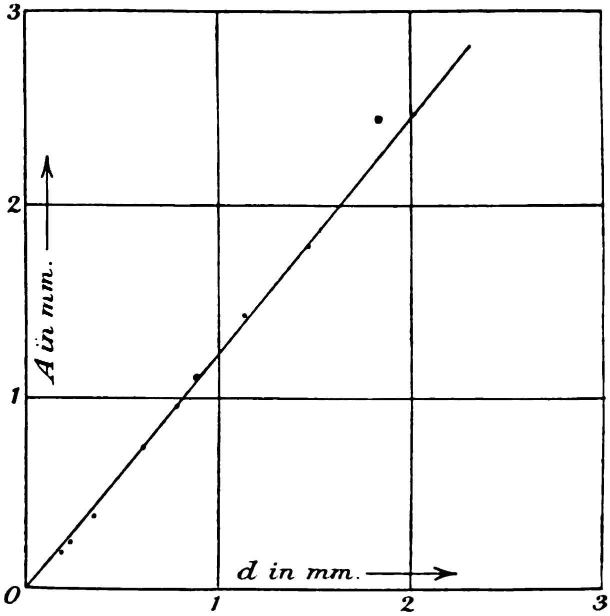


FIG. 7.

the origin (Fig. 7). (The only exception is shown by a value of A found for a very wide slit, $d=0{\cdot}188$ cm.)

From this graph we have

$$A=1{\cdot}22(5)d.$$

The equation is now

$$\frac{1}{v}=\lambda(a_0{}^2-A^2)=\lambda(a_0{}^2-1{\cdot}50d^2)$$

The gradient λ is of the dimensions $\left(\frac{T}{L^3}\right)$. Since λ can only depend on the slit-width d, and on the nature of the gas used, one might assume that its dimensions are $\left(\frac{\rho}{\eta}\cdot\frac{1}{L}\right)$, in which the length is the width of the slit.

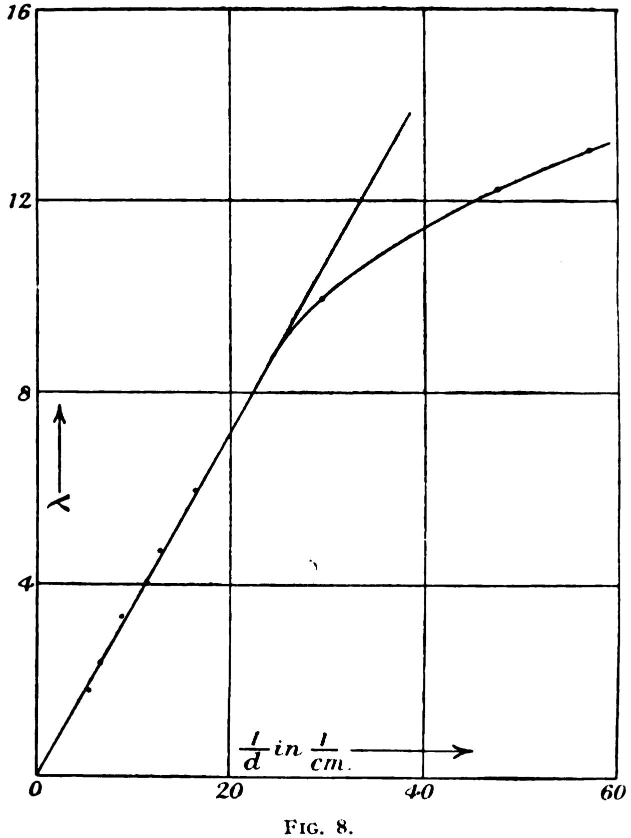


FIG. 8.

Fig. 8 shows the effect of plotting $\frac{1}{d}$ against λ. For all slit-widths greater than

0·035 cm. the relation is that of a straight line passing through the origin. If B be a numerical constant, we have

$$B\frac{\eta}{\rho}\cdot\frac{d}{v}=a_0{}^2-1{\cdot}50d^2$$

or

$$B\left(\frac{\nu}{vd}\right)=\left(\frac{a_0}{d}\right)^2-1{\cdot}50$$

which embodies the principle of dynamic similarity.

F. The Tonal Boundary.

The occurrence of the distance a_0 is due to the departure of the tonal boundaries from the straight lines. If the edge is at a distance a from the slit, an eddy-centre is formed near the slit at a distance

$$\frac{y}{2}=\frac{h}{l}\cdot\frac{a}{2}$$

from the principal plane (Fig. 9). From the boundary maps it appears that normally an eddy formed at a position L moves along the straight line LM, and can be intercepted by the edge at M. An eddy formed at L′, however, can be intercepted by the edge at M″, having moved inwards a distance M′M″ in traversing the distance a parallel to PX. The normal case may correspond to an eddy moving as a roller between air at high and air at low velocity. The abnormal case may be due to the movement of an eddy in a field of forward moving air having a steep velocity gradient at right angles to the direction of motion. To obtain an expression for the force on unit length of a rectilinear vortex of strength M moving in a field of uniform velocity V relative to the eddy centre, Prandtl used the equation

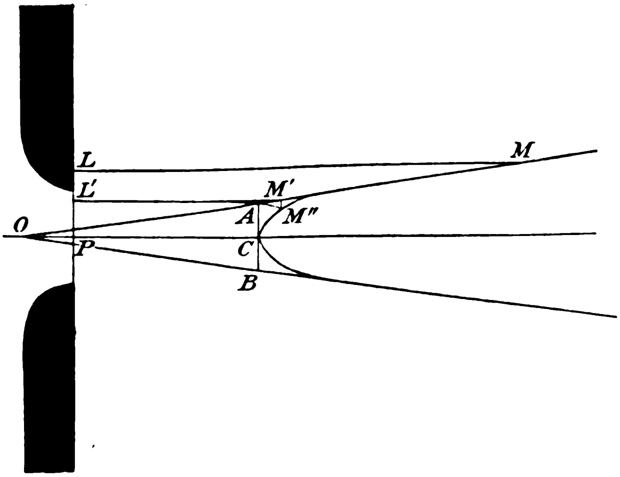


Fig. 9.

(Rate of change of upward vertical momentum)
=(resultant upward pressure on surface of bounding cylinder)
+(resultant upward vertical pressure due to the body—in this case, fluid—within the cylinder),

and hence found that the force per unit length in a direction at right angles to the velocity of the field is $V\rho M$. Using this equation, I find that in a field of uniform velocity-gradient, the acceleration of the eddy at right angles to the velocity field is, to a first approximation, of the form $\left(c_1 MV + c_2 MV\frac{\partial V}{\partial y}\right)$, where V is the velocity of the field relative to the eddy-centre. About a laminar jet $\frac{\partial V}{\partial y}$ is very great, so that it is possible that only the second term is of importance. The frequency observations (to be published later) show that one can assume $\frac{\partial V}{\partial a}=0$. Since M, the eddy-strength, must, in the case of edge-tones, also depend on the total quantity of air leaving the slit per second, we may assume the motion of the eddy to be given by

$$\frac{\partial a}{\partial t}=\text{const.}=aV_0$$

$$\frac{\partial^2 y}{\partial t^2}=KV_0(V-aV_0)\frac{\partial V}{\partial y}$$

where V_0 is the velocity of the fluid in the principal plane (i.e., the maximum velocity of the jet), and the product KV_0 has no dimensions

when $$t=0, y=y_0\,;\ \frac{\partial y}{\partial t}=0\,;\ \frac{\partial a}{\partial t}=aV_0\,;\ a=0.$$

Assume the distribution of velocity about the principal plane to be of the form

$$V=V_0 e^{-ny}$$

where $1/n$ is a length, probably the slit-width.

Then, by two integrations and substitution,

$$\frac{e^{ny}}{e^{ny_0}}=\cos\left(\frac{n}{a^2}\cdot e^{-ny_0}\sqrt{KV_0}\cdot a\right)$$

One might assume $K=\frac{cd}{\nu}$, where c is a numerical constant.

Then when $$y=0,\ a=a_0$$

$$c\cdot\frac{d\cdot V_0}{\nu}\cdot a_0^2=\text{a constant (depending on } n,\ a \text{ and } y_0)$$

which is somewhat similar to the experimental result.

It was therefore desirable to know the exact form of the nose of the tonal boundaries. The distances involved are very small, and the curve approaches the axis $y=0$ very steeply. One source of error, a possible slight transverse movement of the apparatus relative to the edge, was eliminated by plotting the total possible transverse movement y against a.

Fig. 10 shows some of the curves obtained in this way, drawn to a very large scale. The following formula was found to satisfy the shape of the curves for wide slits:—

$$y=\frac{h}{l}\bar{a}-\frac{h}{l}\bar{a}_0 \,.\, e^{-(m^2\bar{a}^2-m^2\bar{a}_0^2)}$$

or

$$ye^{m^2\bar{a}^2}=\frac{h}{l}\left(\bar{a}e^{m^2\bar{a}^2}-\bar{a}_0e^{m^2\bar{a}_0^2}\right)$$

in which $\bar{a}_0$ and $\bar{a}$ denote a_0 and a respectively, *plus* the distances from the pole P to the origin 0.

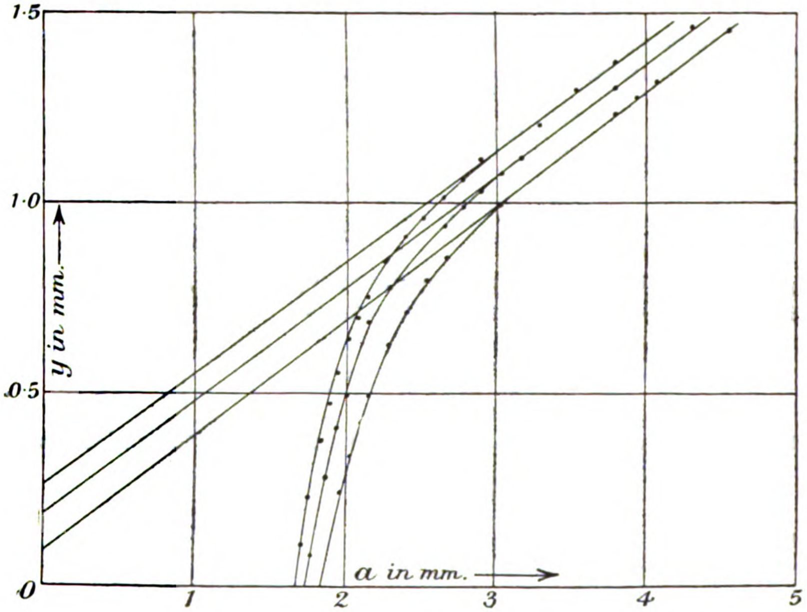


FIG. 10.

a_0 and a were measured from P. $\bar{a}_0$ and $\bar{a}$ are measured from 0.

By plotting $\log_e\left(\dfrac{\frac{h}{l}\bar{a}_0}{\frac{h}{l}\bar{a}-y}\right)$ against $(\bar{a}^2-\bar{a}_0^2)$

(Fig. 11), it is seen that diagrams made with the same slit-width but different pressures yield the same value of m. Moreover, $1/m$ must be dimensionally a length. For very wide slits $1/m$ was found to be very nearly equal to the slit-width. For less broad slits, $1/m$ is always greater than d. For narrow slits this only holds over a small range of $(\bar{a}^2-\bar{a}_0^2)$, after which there occurs a sudden change of gradient (Fig. 12).

G. CONCLUSION.

In the above work a narrow slit has always implied a slit of width less than 0·035 cm. It is strange that this width appears to be absolute for air. Kohlrausch found the same value in his work on slit-tones, exhibiting a demarcation between broad and narrow slits.

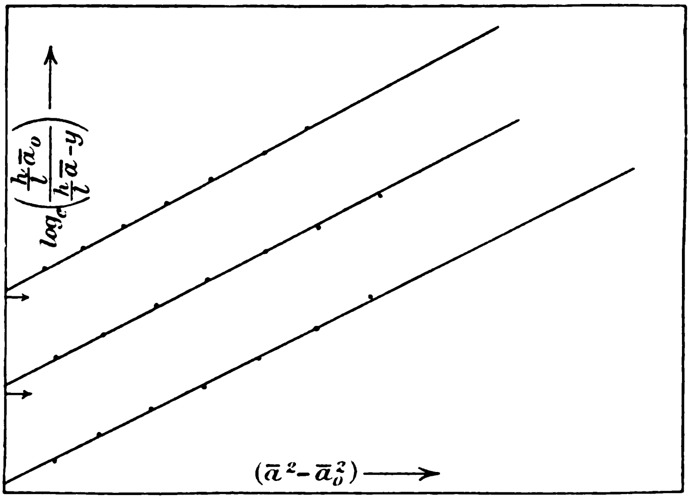


FIG. 11.

The boundary maps, moreover, give further support to the above suggestion of the deflection of an eddy in a steep velocity gradient. We know that when the pressure is increased the whole map advances towards the slit. Since, however, the

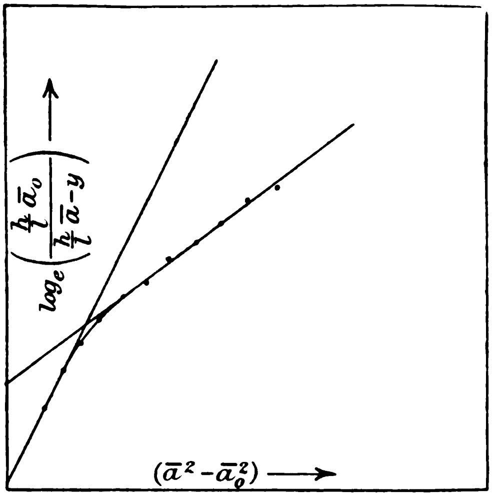


FIG. 12.

slope $\frac{h}{l}$ changes slightly with the pressure, the distance OC (Fig. 9) is not a constant for the slit-width. The maps, however, show that for wide slits the distance AB (the separation of the straight-line boundaries at the nose) is apparently constant. In Table II are given the values of the ratio AB/d for various slit-widths. This means that when the edge is at the distance $a=a_0$ from a wide slit the eddies are being produced at distances about $\frac{0 \cdot 67}{2}d$ on either side of the principal plane, and are being deflected by that entire amount in their passage to the edge. Such eddies, therefore, originate *in the mouth of the slit,* in a field of high velocity-gradient. With narrow slits this field will be less broad, and the range of $(\bar{a}^2-\bar{a}_0^2)$ over which one may hope to find a uniform law of deflection, proportionally smaller. As a is increased, the eddies will originate further from the principal plane, until they move on lines remote from the influence of the slit and are undeflected in their uniform progress.

TABLE II.

d	Pressure in cm. of water	$\frac{AB}{d}$
0·077 cm.	0·34	0·64
	0·62	0·69
0·104 cm.	0·38	0·68
	0·63	0·65
0·133 cm.	0·25	0·68
	0·45	0·68
0·181 cm.	0·14	0·65
	0·29	0·67

In conclusion, I would like to express my gratitude to Prof. S. W. J. Smith for granting me such excellent facilities for the execution of these experiments, and for his encouragement during the course of the work.

BIBLIOGRAPHY.

R. Wachsmuth, Verh. phys. Gesel., 5, p. 299 (1903); Phys. Zeitschr., 4, p. 743 (1903); Ann. d. Phys., 14, p. 469 (1904).

Wachsmuth and Kreis, Verh. phys. Gesel., p. 60 (1906).

M. Weerth, Ann. d. Phys., 11, p. 1086 (1903).

V. Hensen, Ann. d. Phys., 2, p. 719 (1900); Ann. de Phys., 4, p. 41 (1901); Ann. d. Phys., 16, p. 838 (1905); Ann. d. Phys., 21, p. 781 (1906).

C. Sondhauss, Pogg. Ann., 124, pp. 1, 135 (1865); Pogg. Ann., 91, pp. 128, 214 (1854).

V. Strouhal, Wied. Ann., 5, p. 216 (1878).

W. Kohlrausch, Wied. Ann., 13, p. 545 (1881).

H. R. Göller, Dissertation, Giefzen (1912).

W. König, Phys. Zeitschr., 13, p. 1053 (1912).

E. Schmidtke, Ann. d. Phys., 60, p. 715 (1919).

J. Rieth, Dissertation, Giefzen (1917).

Th. von Kármán, Göttinger Nachr., p. 547 (1912).

Th. von Kármán and H. Rubach, Phys. Zeitschr., 13, p. 49 (1912).

Lord Rayleigh, " Theory of Sound," 2nd ed., Vol. II, p. 372 (1896) ; Phil. Mag., 29, p. 435 (1915).

P. Cermak, Phys. Zeitschr., 25, pp. 121-130 (1924) ; Phys. Zeitschr., 23, pp. 394-397 (1922).

Z. Carrière, Jour. Phys. et Rad., p. 52, February (1925).

DISCUSSION.

Sir **Richard Paget** said that the author's work might be of great value in connexion with the design of organ pipes. It is a curious fact that if the walls of the channel leading to the jet-orifice are smooth the tone obtained is not so good as that given by rippled walls.

Dr. W. S. **Tucker** complimented the author on his painstaking work, which has opened the way for further research. As a source of sound for experimental purposes the organ pipe has proved very unsatisfactory, as its behaviour is to a great extent incalculable. The jet as a source of sound is coupled with the pipe as a resonator, and the reaction between the two presents a complicated problem ; and then any variation in the velocity of the jet will affect the rate of production of eddies. The quality and intensity of the resulting tone depends on all these factors, and the present Paper should point the way to a better understanding of the mechanism of the process.

Dr. G. W. C. **Kaye** said that at the National Physical Laboratory the organ pipe has had to be abandoned as a source of sound. Possibly the author might be able to improve the design of such pipes so as to render them suitable for laboratory use.

Mr. E. G. **Richardson** said that about a year ago he read a Paper to the Society on a somewhat similar subject ; he had employed the method of Kruger, who, however, had been unable to get results. The Paper in question was devoted to a study of æolian tones, and an annular jet was employed, as opposed to the author's ribbon-shaped jet ; but curves similar to those of the author's Fig. 4 were obtained for jets of smoke and water. The author's measurements are some of the most careful that have been made, and he has followed a new line of inquiry, as previous experiments have dealt mainly with the question of frequency. His plan of measuring the depth of the jet is a very sound one. Although Kármán first applied the eddy theory to experimental work, credit must also be given to Bénard, who put it forward seven or eight years earlier. As regards the streamlining of the author's orifices, this plan would affect the value of a_0, in consonance with results obtained by the speaker and Mr. Tyler. There is rather a puzzling connexion between the frequency and the distance of the edge from the orifice ; the distance between the eddies appears to adapt itself to this distance. No very satisfactory explanation of this phenomenon has been offered.

Mr. E. **Tyler** (communicated) : With reference to this very interesting Paper I should like to congratulate the author on his very careful work in dealing with such a difficult problem, and I should furthermore like to point out that in his determination of small tonal boundary measurements he claims to measure these to ·00025 cms., whereas the accuracy of movement of the wedge is about ·001 cm. On what assumptions does the author claim such accuracy of small measurements ? Has the author tested microscopically for any vibration of the support that might occur during the production of the edge-tones, for with such a wedge as used by the author there is a possibility of Æolian Tone phenomena.

The results shown in Fig. 4 are very interesting indeed and resemble similar characteristic liquid jet curves published by Dr. Richardson and myself (Proc. Physical Society, August, 1925). I rather regret the author has plotted values of a_0 (minimum) against the pressure (cms. of water), for a better comparison no doubt could be made by plotting a_0 against v. (vel. of air steam). Has the author considered whether viscosity is a factor modifying the shape of these curves, and if so, what are his views ?

Referring to Fig. 5, I do not see any justification in continuing the curves back in such a manner so as to cut the $\frac{1}{\sqrt{p-p_0}}$ axis below 0 at points where $a_0=0$ giving a value for $\frac{1}{\sqrt{p-p_0}}=-f$.

Unless to satisfy the condition shown in Fig. 6, i.e., the $\sqrt{\frac{1}{\sqrt{p-p_0}}+f}$, a_0 curves all intercept at the origin. There is no reason why the curves in Fig. 5 could not be all continued to cut at one point below 0 at a constant f. This result would thus modify the curves in Fig. 6.

AUTHOR'S reply: I am very grateful for these comments and criticism on my Paper. Sir Richard Paget has mentioned the design of the throat of an organ-pipe. I am aware of the practice of "nicking" the slit, but organ-builders only perform this operation on pipes of certain stops, to which it is supposed to impart rapidity and brightness of speech. The practice must have an important bearing on the production of edge-tones, but at present I have made no experiments in this direction.

Dr. Tucker and Dr. Kaye have spoken of the unreliability of the organ-pipe as a standard source of sound. This is not unavoidable, but I can see no prospect of a pipe ever being made which will compare favourably with a standard fork. The degree of coupling between a pipe and the edge-tones formed at its mouth has been examined very ably by Prof. Camière at Tours (Journ. Phys. et Rad., Février, 1925).

I am glad that Dr. Richardson has raised the question of Bénard's work in relation to vortex-systems. In calling the arrangement a Kármán system I am only following Prandl's school who quite rightly give Kármán the credit of having established the theory of this system, without wishing in the least to depreciate the value of Bénard's experiments and observations. By streamlining the slit a jet was obtained of an ideally simple type, and any change in the values of a_0 obtained by this method must be a change for greater simplicity. The question of frequency will be dealt with in the second Paper.

In thanking Mr. Tyler for his communication I regret that my brief statement of the accuracy of movement of the edge should lead to misunderstanding. The *total* error of the screws over so great a distance as 1 cm. may be as great as ·001 cm., but over the minute distances measured in the tonal boundaries, the error did not exceed ·00025 cm. My assumption of such accuracy is based on comparative measurements at different positions on the screws, over two thousand observations having been made in the measurements of these tonal boundaries alone.

Mr. Tyler is mistaken in believing that Æolian phenomena may ever arise behind the forward edge of a surface parallel to the direction of flow. A necessary condition for Æolian tones is freedom for the eddies formed on one side of the obstacle to move under the influence of the eddies liberated on the other side. With a wall boundary that is impossible. There is a very simple and absolutely sure method of testing for vibration in the edge. On placing the fingers on the side of the edge no change in the pitch or quality of the tone occurs. Nor are the values of a_0 and y affected. It is recognized that a light touch by the fingers will immediately damp out all vibrations except those of very high frequency in great thickness of metal.

Mr. Tyler will find the answers to his questions concerning velocity and viscosity in the Paper itself. I fail to understand his suggestion that a given family of experimental curves may be produced at will to pass through a given point, since if a curve is to retain the character given by experiment it may only be produced in one way. This has been done in Fig. 5. Nor was it necessary to obtain the values of "f" for the determination of the equation of dynamic similarity, as the values of A yield the same result. I trust that a second Paper will bring out the relative importance of the different factors with more clearness than has been possible in this first communication.

XV.—THE SPECTROSCOPIC DETECTION OF MINUTE QUANTITIES OF MERCURY.

By J. J. Manley, *M.A.*, Research Fellow, Magdalen College, Oxford.

Received October 18, 1925.

ABSTRACT.

Details are given of a method whereby vertical spectrum tubes (demanded by certain investigations) can be critically examined for vanishingly small quantities of mercury. The tubes have two U-limbs partially immersed in insulated water. The water serves as external electrodes. An end-on view of the glow within the excited tube is obtained by a totally reflecting prism formed upon the summit of one of the limbs. The light is thus deflected horizontally and received in the usual way by a spectrometer.

RECENTLY I have found it necessary to examine spectroscopically the low pressure and gaseous contents of some U-tubes for minute quantities of mercury.

The U-tubes, having a length of 24 cms. and an internal diameter of 1·2 mm. or less, formed parts of some permanent apparatus; and, owing to the conditions required for experimenting, the tubes were of necessity situated vertically. Under those circumstances, the only view obtainable with a Hilger wavelength spectrometer was one at right angles to the axis of the tube, and this was not always sufficiently sensitive. A further difficulty arose from the fact that internal electrodes for producing a discharge were not permissible. The weight of the mercury that might be present varied from a maximum of 0·0002 grm. to a quantity vanishingly small. Initially, the plan adopted was that indicated in Fig. 1.

A and B_1 represent two U-tubes, each having the dimensions noted above. The mercury was sought for in the tube B_1. External electrodes were provided by the partial immersion of the tubes in water contained in the insulated beakers *C*, *D*. Wires from the high potential terminals of the induction coil *I* were led into the contents of *C* and *D*. When the coil was activated with a 6-volt accumulator *G*, the limbs *j*, *k* were filled, like an ordinary spectrum tube, with a bright glow; hence any section of *k* could be examined with the spectrometer. This simple device proved amply sufficient for all those cases in which the mercury present in *k* attained or exceeded some as yet undetermined limit; the plan, however, failed when the weight of the element in the tube was infinitesimal. For aiding in the detection of excessively small quantities, the modified U-tube B_2 shown in Fig. 2 was designed. It was constructed as follows:

First a T-piece was made, and one of its three limbs shortened to 3 mm. The short limb was then closed by a glass rod which was fused to it. During the fusion the work was so conducted that the attached end of the rod presented a flat surface within. Next, the rod was melted and rotated in a blowpipe flame until it had assumed a form almost truly spherical.* After annealing, two plane faces were by means of carborundum powder and turpentine, ground upon the sphere ; one of these (α) was vertical, the other (β) intersected α as shown, at an angle of 45°. Each face was then smeared with Canada balsam and covered with a thin glass plate. The required plates were cut from a cover slip used for work with the microscope. Made thus, the totally reflecting glass prism P was extremely satisfactory. Finally, the long limb k of the T-piece was bent U-wise, as seen in Fig. 2, and the whole substituted for the simpler tube B_1 of Fig. 1. By placing the spectrometer slit near the face α and activating the coil, an end-on view of the glow in k is obtained by reflection, and spectral lines otherwise invisible or but feebly seen are revealed more or less prominently.

---

* A suitable sphere is one having a radius of 5 mm. The length of glass rod required for its production is calculated at the outset. The complete sphere is indicated by the dotted line.

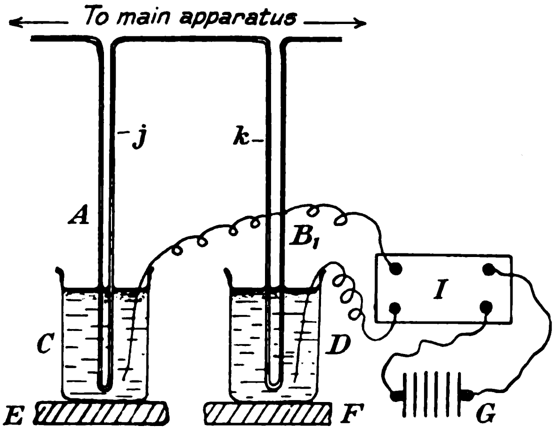


Fig. 1.

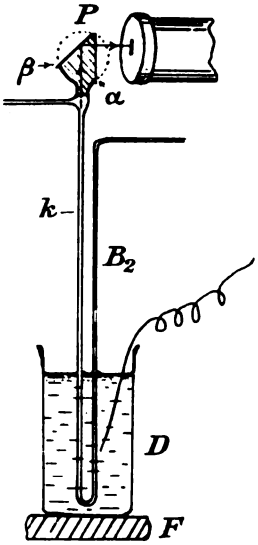


Fig. 2.

XVI.—ON THE STORAGE OF SMALL QUANTITIES OF GAS AT LOW PRESSURES.

By J. J. MANLEY, *M.A.*, Research Fellow, Magdalen College, Oxford.

Received November 11, 1925.

ABSTRACT.

The author describes and gives a figure of an apparatus used for storing small quantities of rare or highly purified gases in such a way that contaminating air is excluded The apparatus is designed for use in conjunction with a Sprengel pump, which withdraws the gas from any experimental plant and delivers it into the storage apparatus. With the aid of barometric traps, etc., the gas can be readmitted either partially or wholly into the experimental plant.

DURING a research conducted with pure helium at pressures varying from 1-12 mm. of mercury, it has frequently been necessary to modify the experimental apparatus. At the outset the helium was on each occasion first withdrawn by a Sprengel pump and collected in a tube; subsequently it was returned to the apparatus by means of a specially constructed pipette. In every instance after the re-introduction of the helium a spectral analysis revealed the presence of decided traces of air. If the apparatus had been small and compact, the impurity could have been quickly removed by circulating the gases over charcoal cooled by liquid air; but in the present case the primary portions of the apparatus were connected by tubes having capillary dimensions and great length, also the total volume of the apparatus was considerable; hence much time was required for completing the absorption of the contaminating gas. Ultimately this difficulty was avoided by the use of the storage apparatus depicted in Fig. 1. From the figure it may be seen that the apparatus communicates (*a*) with the main or experimental apparatus through the tube m, to which it is fused, and (*b*) with a twinned barometric column R, and that the whole in conjunction with the main apparatus can be evacuated by a Sprengel pump P.

The highly purified helium was at the first introduced by way of the limb β, the mercury trap J being open; a similar trap K was either open or closed as circumstances demanded (*vide infra*). For effecting alterations in the form of the experimental apparatus the procedure is as follows.

First the trap J is closed by raising the cistern E, so that the mercury attains some such level as a . . . . b; the tap t_1 is then shut. Next, the open end of the limb β is placed over the jet of the fall-tube of the Sprengel pump as shown. This operation is rendered possible and perfectly safe by the flexibility of the upper connecting tubes, which are long and narrow. The pump is now brought into action, and the gas thus transferred from the experimental to the storage apparatus. The helium having been removed, the limb β is withdrawn from the jet and the main apparatus filled with dry and carbon dioxide-free air. With the entry of the air, the mercury in the trap J rises to something less than barometric height in the tube above *b*. The desired alterations in the main apparatus may now be undertaken, and when completed the whole apparatus is again highly evacuated. On lowering

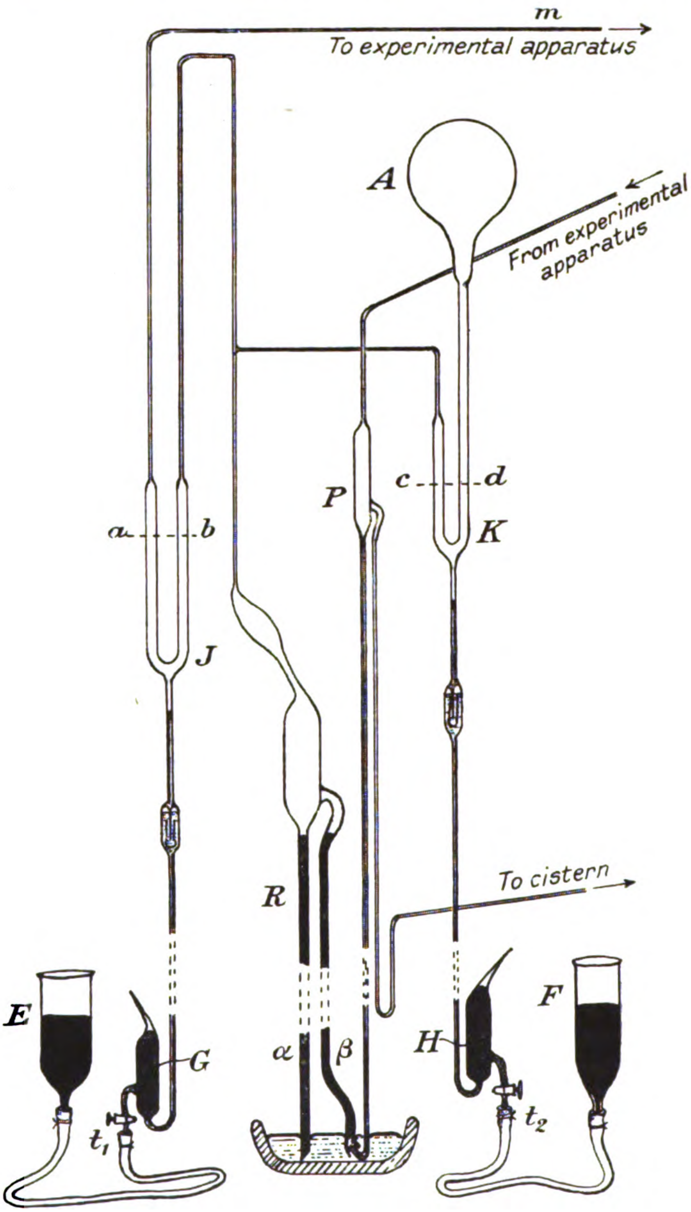


FIG. 1.

the cistern *E* and opening the tap t_1, the trap *J* is freed from mercury and the stored gas flows back into the apparatus for further experiments.

It may be noted that the effective volume of the storage apparatus depicted in Fig. 1 can be varied. If the volume of the gas to be stored is relatively small, the bulb *A* is not required. In that case *A* is trapped off by raising the cistern *F* so that the mercury stands at the level *c . . . d*, and the tap t_2 closed. Again, if for new experiments to be carried out after the storage and subsequent release of the gas, a portion only of the helium is required, the trap *K* is kept open whilst the gas is being stored, and then closed before *J* is opened. If necessary, the quantity of the gas in the experimental apparatus can at any moment be increased by suitably manipulating the cistern *F*.

XVII.—THE EFFECT OF ROLLING ON THE CRYSTAL STRUCTURE OF ALUMINIUM.

By E. A. OWEN, *M.A.*, *D.Sc.*, and G. D. PRESTON, *B.A.*, Physics Department, National Physical Laboratory.

ABSTRACT.

Sheets of aluminium have been examined by the ionisation spectrometer and by photographic methods, with a view to discriminating between two contradictory results obtained by previous observers with the photographic method as to the final orientation of crystals in rolled material.

The results show that, when a cast specimen of aluminium containing a number of large crystals oriented at random throughout the body of the material is rolled, the crystals break up into a large number of minute crystals. As the thickness of the material is progressively diminished, the small crystals tend to take up a definite orientation, each crystal having a cube diagonal in the direction of rolling and a (211) plane in the plane of rolling. Two sets of crystals exist in the material after rolling, the one set being the optical image of the other in the plane of rolling.

The observations obtained by the ionisation spectrometer indicate that the type of the space lattice remains unaltered, and that the parameter of the material in the severely worked condition does not differ from that of the annealed material by more than 0·5 per cent.

INTRODUCTORY.

THE orientation of the crystals in rolled aluminium sheets of thickness 0·015 mm. has been examined by Mark and Weissenberg,[*] who concluded that in the rolled condition the crystals were oriented with a (110) plane parallel to the plane of rolling with a divergence of ±35° and a (112) direction parallel to the direction of the rolling with a divergence of ±8°. This arrangement places the cube diagonal (111) in the surface of the foil perpendicular to the direction of rolling, as in Fig. 1*a*. Further work on the same subject by Wever[†] led him to the conclusion that a (111) direction lay parallel to the direction of rolling, a (110) parallel to the transverse direction, and a (112) parallel to the foil normal, as in Fig. 1*b*. These discordant results were obtained by photographic methods.

The experiments, a description of which follows, are now published with a view to discriminating between the above conclusions. Sheets of aluminium have been examined by the ionisation spectrometer and by the photographic method, the former having the advantage that direct measurements can be made of the angles between planes in the same zone.

I. EXPERIMENTS WITH THE IONISATION SPECTROMETER.

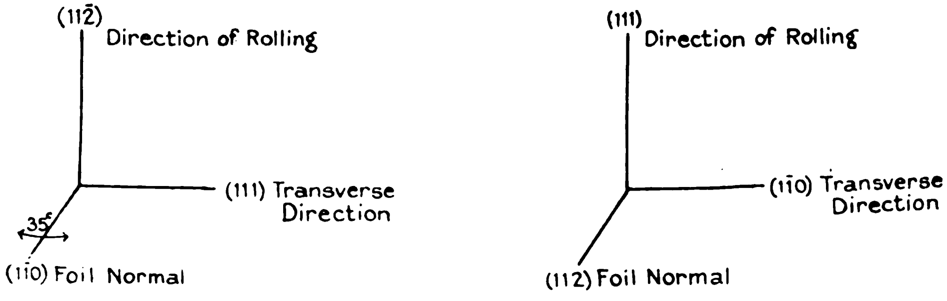
Examination of Cast Specimen of Aluminium.

The crystal grains in the etched surface of the specimen of cast aluminium (1·06 cm. thick, 2 cms. wide and 6 cms. long) employed, were about 1 to 2 mm. across. The specimen was mounted on the spectrometer table with its length parallel to the axis of the instrument, and its surface parallel to the incident beam of X-rays from a molybdenum anticathode. The widths of the bulb, crystal and chamber slits were 1 mm., 4 mm. and 0·5 mm. respectively. The chamber was set at the appropriate angle to receive reflections from the (111) planes. The crystal table was rotated, and readings of the intensity were taken at intervals of $\frac{1}{4}$°. This procedure was repeated with the ionisation chamber set to receive the reflections from the (100), (110) and (311) planes. The results are shown in Fig. 2, the peaks representing the effect of the single crystals as they are brought successively into the reflecting position by the rotation of the specimen.

---

[*] Zeitschrift für Physik., 14, p. 328 (1923), and 16, p. 314 (1923).

[†] Zeitschrift für Physik., 28, p. 69 (1924).


(11$\bar{2}$) Direction of Rolling
(111) Transverse Direction
35°
(1$\bar{1}$0) Foil Normal
(111) Direction of Rolling
(1$\bar{1}$0) Transverse Direction
(11$\bar{2}$) Foil Normal

(*a*) (*b*)

FIG. 1.

Examination of Rolled Specimen after a 14·2 *per cent. Reduction in Thickness.*

The specimen was now marked by means of saw cuts on the edges, so that after rolling the same region could be again examined. The thickness was reduced from 1·06 cm. to 0·91 cm., and the above observations repeated with the direction of rolling parallel to the spectrometer axis and the chamber set to receive the rays reflected from the (111), (100) and (110) planes as before. The results are shown in Fig. 3*a*, and it will be seen that the intensity curves no longer show a series of sharp maxima and minima, but are approximately smooth, showing that the large crystals

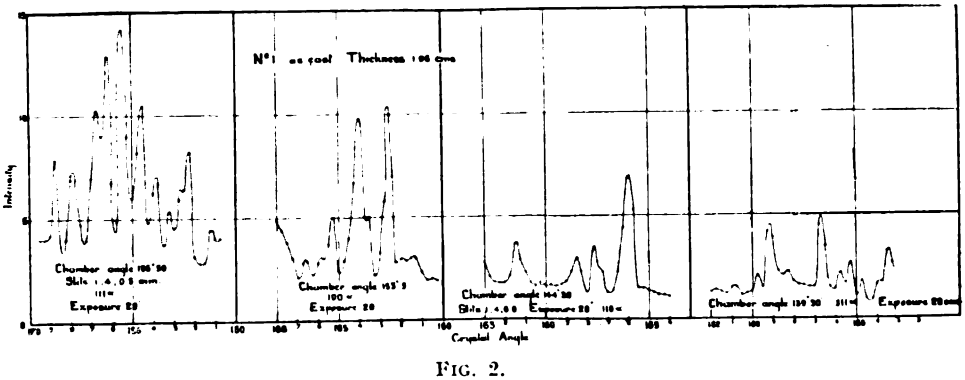


FIG. 2.

originally present have been broken up into a large number of minute crystals. The surface of the specimen was now deeply etched, and the observations repeated with a view to ascertaining whether the effect was present throughout the mass of the material or whether it was localised on the surface. It was found that etching did not alter the nature of the curves already obtained, so that the breaking up of the large crystals takes place, if not right through the material, at any rate to very considerable depth—of the order of at least a few millimetres.

Examination of Rolled Specimen after Successive Reductions in Thickness ranging from 57·5 *per cent. to* 99·0 *per cent.*

The rolling was proceeded with, and similar observations taken at thicknesses of 0·45 cm., 0·23 cm. and 0·01 cm. The intensity of the reflections diminished as the thickness of the specimen decreased, so that the chamber slit had to be opened to 2 mm. for this series of observations. The only new fact observable from these curves is that the intensity of the (110) and (311) reflections becomes gradually greater, and finally exceeds the intensities of the (111) and (100) reflections, as shown in Fig. 3 (*b*, *c* and *d*). The same fact is also illustrated in Fig. 4, which shows parts of the spectrum obtained from the surface of the metal when reduced to the thicknesses above mentioned, the chamber in this case being rotated at twice the rate of the crystal. The relative diminution of intensity of the (100) reflections is particularly marked. In the specimen of thickness 0·01 cm. (Fig. 4*c*), the (111) reflec-

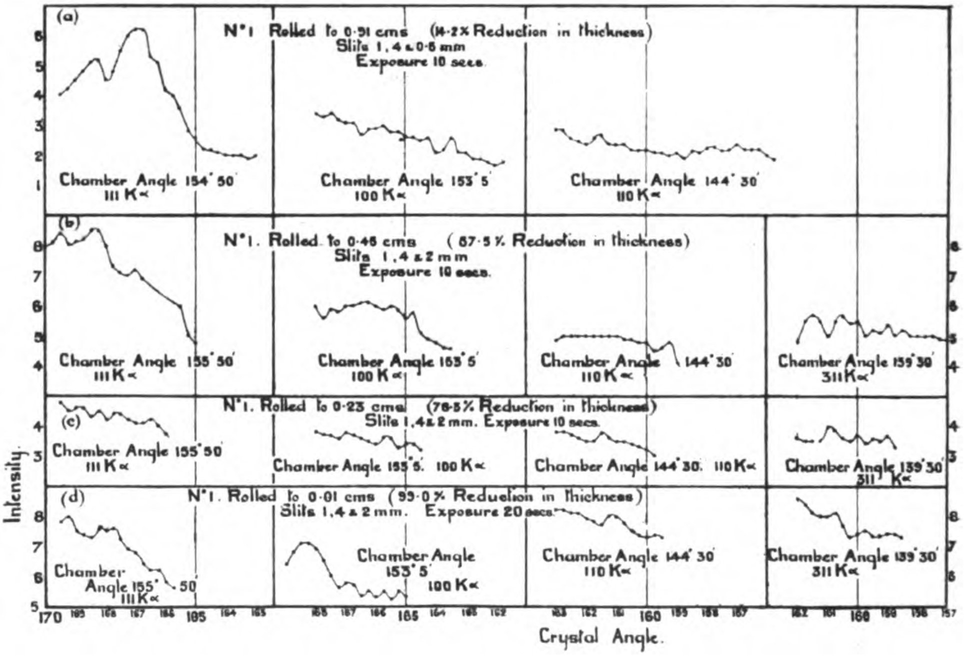


FIG. 3.

tions are comparatively feeble and displaced, (100) is hardly discernable, while (110) and (311) are both intense. In all specimens of this thickness which we have examined the (100) reflections from the surface are absent. The (111) reflections are always displaced about ½° towards the origin, and (110) and (311) reflections are particularly intense and in their correct positions. The value of the parameter, as determined from the observed reflections, does not differ from that of aluminium in the unworked state. The results obtained from the observations of Fig. 4 are given in Tables I, II and III, and show that the parameter of the lattice has remained unaltered.

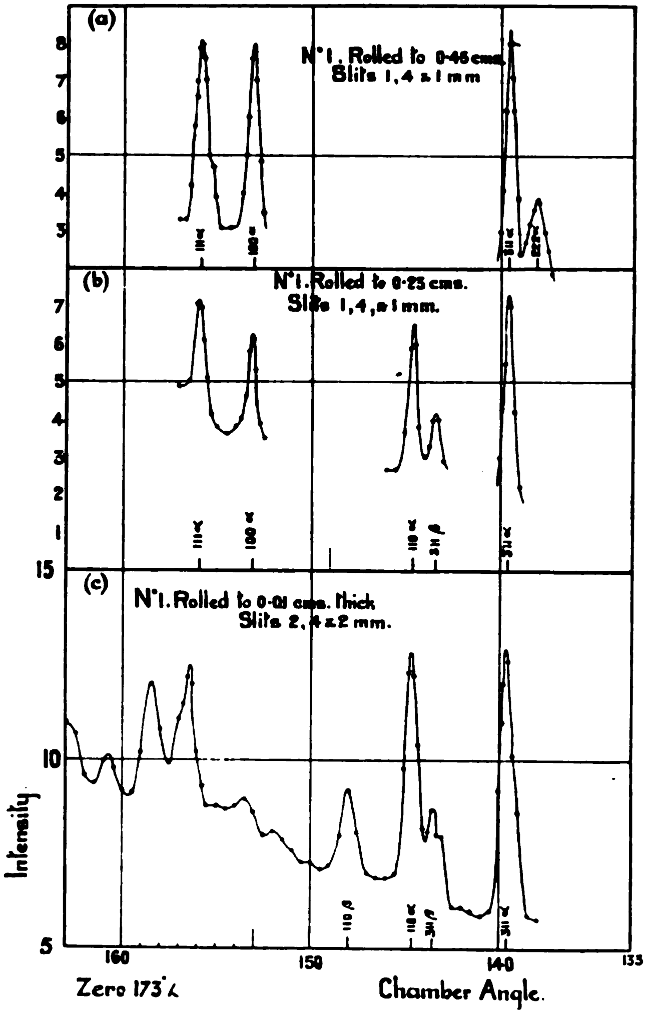


FIG. 4.

TABLE I.

Thickness=0·45 cm. (Fig. 4*a*). $K\alpha=0{\cdot}7078$Å.
$K\beta=0{\cdot}630$Å.

Reading of intensity maximum.	Glancing angle θ	Form.	λ	Sin θ	a
155°53′	8°43′	111	$K\alpha$	0·1515	4·046Å.
153 6	10 6	200	$K\alpha$	0·1754	4·036
139 33	16 53	311	$K\alpha$	0·2904	4·042
138 6	17 36	222	$K\alpha$	0·3024	4·053
					Mean $a=4{\cdot}044$Å.

TABLE II.

Thickness=0·23 cm. (Fig. 4*b*).

Reading of intensity maximum.	θ	Form.	λ	Sin θ	a
155°57′	8°40′	111	$K\alpha$	0·1507	4·067Å.
153 9	10 4	200	$K\alpha$	0·1748	4·049
144 38	14 20	220	$K\alpha$	0·2476	4·043
143 23	14 58	311	$K\beta$	0·2582	4·047
139 34	16 52	311	$K\alpha$	0·2901	4·046
					Mean $a=4{\cdot}050$Å.

TABLE III.

Thickness=0·01 cm. (Fig. 4*c*).

Reading of intensity maximum.	θ	Form.	λ	a
144°37′	14°20′	220	$K\alpha$	4·042Å.
139 36	16 51	311	$K\alpha$	4·049
				Mean $a=4{\cdot}045$.

The results agree with each other to 0·25 per cent., which is within the limits of accuracy of the observations.

The peculiarities of the spectrum shown in Fig. 4*c* are typical of the material when reduced to a thickness of 0·01 cm., and are not to be ascribed to any change in the type or in the dimensions of the space lattice. They can be explained by supposing that the crystals of which the metal is composed are all orientated in a particular direction.

In the experiments just described the direction of rolling was vertical, i.e., parallel to the axis of the spectrometer.

Examination of specimen with direction of rolling horizontal.

Five of the sheets of thickness 0·01 cm. were laid flat on one another and mounted on the spectrometer table with the direction of rolling of each sheet lying in a horizontal plane. The chamber of the spectrometer was set to receive reflections from the (111) planes and the specimen rotated. A maximum of intensity was found with the specimen nearly perpendicular to the incident beam, and the best position of the chamber was found to be at 157·25° (16°3′ from the direct beam). The peaks obtained with this chamber setting are shown in Fig. 5*b*. The shift of the (111) peak from 17°23′ to 16°3′ can in this case be accounted for by the divergence of the primary and reflected beams, the bulb and crystal slits being at 2 mm. and 4 mm. respectively and separated by 7 cms. When these slits were cut down to 1 mm. each, the displacement of the peak was reduced to 12′.

The width of the middle peak is about 40°, a few degrees of which are accounted for by the angular width of the incidient beam. Part of the width of the peak might also be due to the sheets of which the specimen was composed not being parallel to one another. As it was impossible to fix the thin sheets together so that they were rigorously parallel, it was decided to continue the work with fresh material rolled from 1 cm. to 0·05 cm. in thickness.

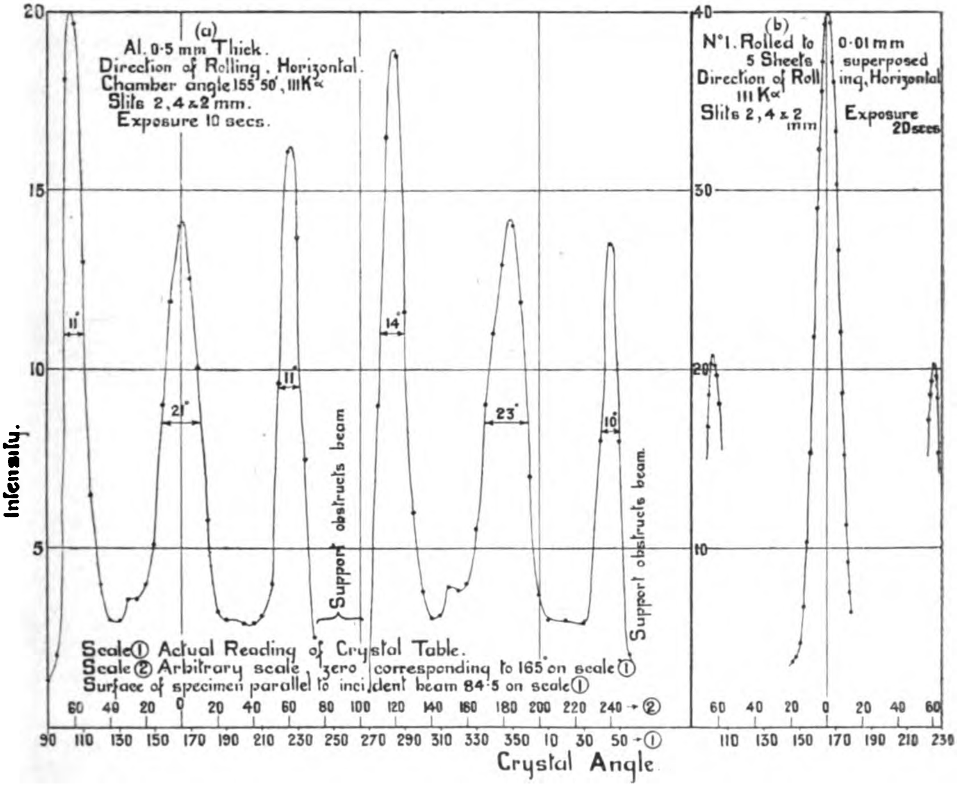


FIG. 5.

Experiments with rolled aluminium sheet 0·05 *cm. thick. Direction of rolling horizontal.*

(A) *Rotation of specimen about a vertical axis.*—A sheet of aluminium was rolled down to a thickness of 0·05 cm., being passed through the rolls always in the same direction. A plate of the material was mounted on the spectrometer with its surface in a vertical plane and with the direction of rolling horizontal as before, the chamber set at the proper angle (155°50′) to receive the (111) reflections and the specimen rotated, readings being taken every 5°. The observations were repeated with the ionization chamber set to receive the (100) and (110) reflections. The results of the three series are shown in Figs. 5*a*, 6*a* and 6*b*.

The second peak from the left of Fig. 5*a* occurs at an angle of 166° on the scale of the crystal table. The angle of reflections from the (111) planes of aluminium is 8·7°, so the planes giving this peak are on the average parallel to the incident beam when the reading of the crystal scale is 174·7°. The surface of the sheet is parallel to the incident beam at a scale reading of 84·5°, so that at a scale reading of 174·7° the surface is inclined at 90·2° to the beam. This set of (111) planes is accordingly at right angles to the surface and to the direction of rolling. Observations taken on this set of planes with other specimens corroborate this result. For example, in the case illustrated in Fig. 5*b* the crystal setting for the same maximum was 165·5° with the same surface zero and in two other cases the figures were 163° and 168°. The figures are in agreement with one another within the limits of accuracy of experiment.

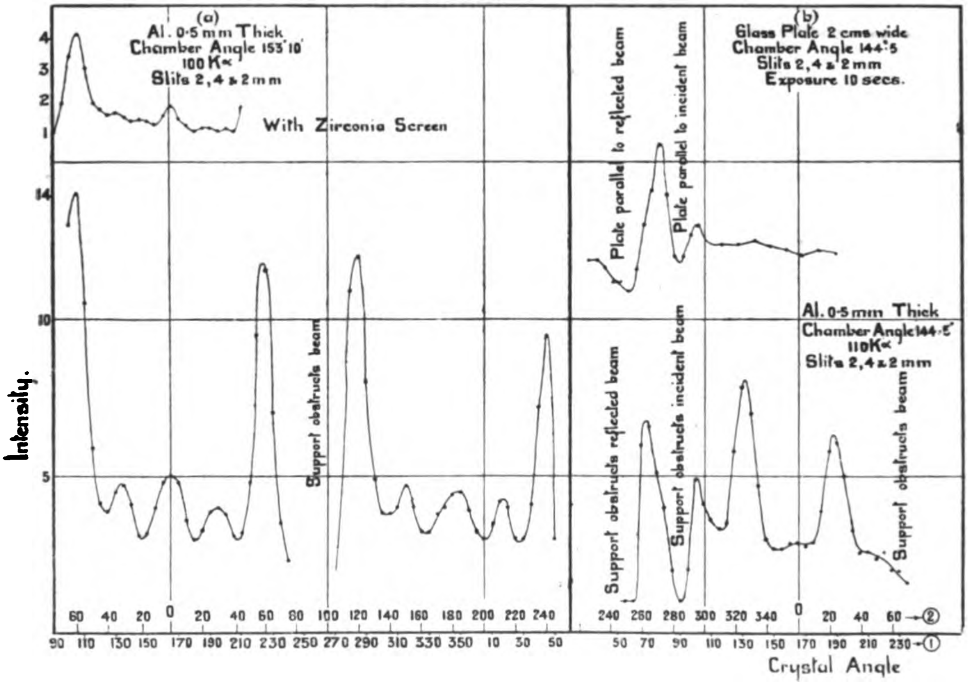


FIG. 6.

It will be convenient to measure the angles of the other planes, fixing this (111) plane as zero. Starting from this plane then, we have in Fig. 5*a* maxima at the following angles :—

0°, 62°, 118°, 184°, 241°, and 297°.

The last three being separated from the first three by approximately 180°, are the reflections from the " back surfaces " of the same sets of planes.

(B) *Rotation of specimen about horizontal axes.*—The specimen was mounted on a frame capable of rotation about two axes perpendicular to each other and to the axis of the spectrometer; one of these axes (A), Fig. 7, was coincident with the direction of rolling and therefore perpendicular to the (111) planes occurring at 0° on the arbitrary crystal scale just mentioned. By setting the specimen in the position to give reflection 0° and rotating it about the A axis, the planes giving the maximum are rotated about their normals and should remain in the reflecting position during rotation of the specimen. This was found to be the case, as shown in the following table:—

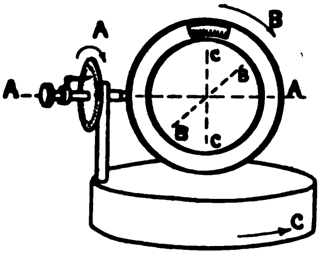


Fig. 7.

Reading of A	−20°	−10°	0°	10°	20°	160°	170°	180°	190°	200°
Intensity	9·8	9·9	10	10	9·1	11·0	11·0	11·1	11·1	11·0
	Exposure 20 secs.					Exposure 30 secs.				

When the reading of A is 0° the surface of the specimen lies in a vertical plane. The intensity of reflection is therefore not sensibly affected by the rotation of the specimen about this axis, but, as the following table shows, it is very sensitive to rotation about the axis B (Fig. 7) perpendicular to the plane of the sheet:—

Reading of B	−20°	−10°	0°	+10°	+20°
Intensity	2·6	6·0	8·6	8·0	5·0

The direction of rolling is horizontal when the reading of B is 0°, the intensity being a maximum when B≑0° and B≑180°.

During the above readings the crystal table stood at 168°. This was now altered to 98°, i.e., the crystal table was rotated through 70°, the angle between the (111) planes being 70°32′. The axis B was set at 0°, so that the direction of rolling was horizontal and readings were taken as the specimen rotated about the A axis. Two very intense maxima, corresponding to readings of A equal to —5° and +185° were observed, the relevant readings being as follows:—

Reading of A	−60°	−40°	−20°	−10°	0°	10°	20°	30°
Intensity	6·2	9·3	9·5	14·0	17·4	11·1	6·5	6·3

Reading of A	150°	160°	170°	180°	190°	200°	220°	240°
Intensity	10·6	11·2	14·6	24·0	26·3	20·0	13·9	9·1

This means that if the first maximum occurring at A$\doteqdot$0° is due to planes inclined at $+\alpha°$ to the surface, the second (A$\doteqdot$180°) is due to planes inclined at $-\alpha°$ to the surface. Or, in other words, there are two sets of crystals in the material, the one being the optical image of the other in the plane of rolling. Further, it appears that the position of best reflection is again with the surface of the sheet in a vertical plane—so that the axis of the spectrometer must be parallel to the line of intersection of two (111) planes, i.e., to the diagonal of a cube face.

Discussion of the results.

The foregoing results indicate that the crystals in the rolled specimens tend to set themselves with a cube diagonal in the direction of rolling and the diagonal of a cube face in the surface perpendicular to the direction of rolling. This arrangement brings a (211) face into the surface of the sheet. Fig. 8 will make this clear;

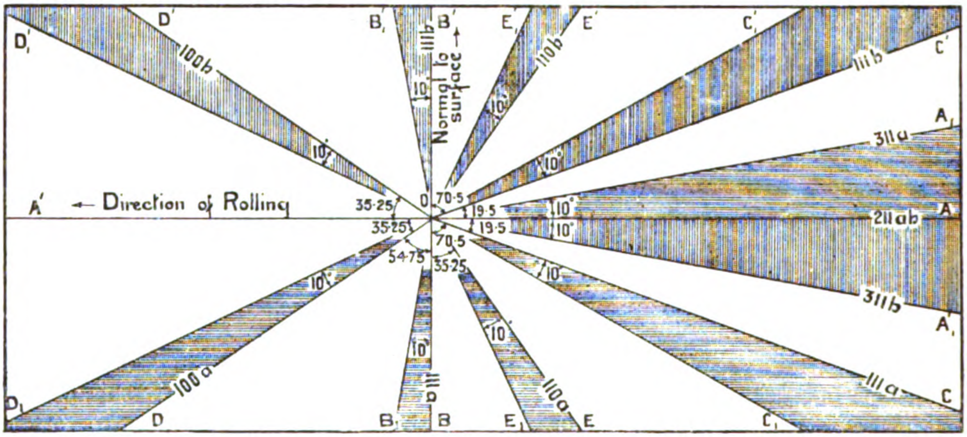


FIG. 8.

in it AOA′ represents the direction of rolling, BOB′ the normal to the surface of the specimen. The axis of the spectrometer in the experiments just described passes through O and is perpendicular to the plane of the diagram. The line OB represents the (111) plane at 0° which we have found to be perpendicular to the plane of rolling. There will then be a (111) plane, which cuts the plane of the diagram in the line OC, the angle BOC being 70°32′. From what has just been said there will also be crystal planes which are the reflections of these in the surface of the specimen—so we put lines OB′ perpendicular to A and A′ and OC′ inclined at 70°32′ to OB′. We then have the (111) planes occurring at the following angles as the specimen is rotated about the spectrometer axis, starting from OB=0°,

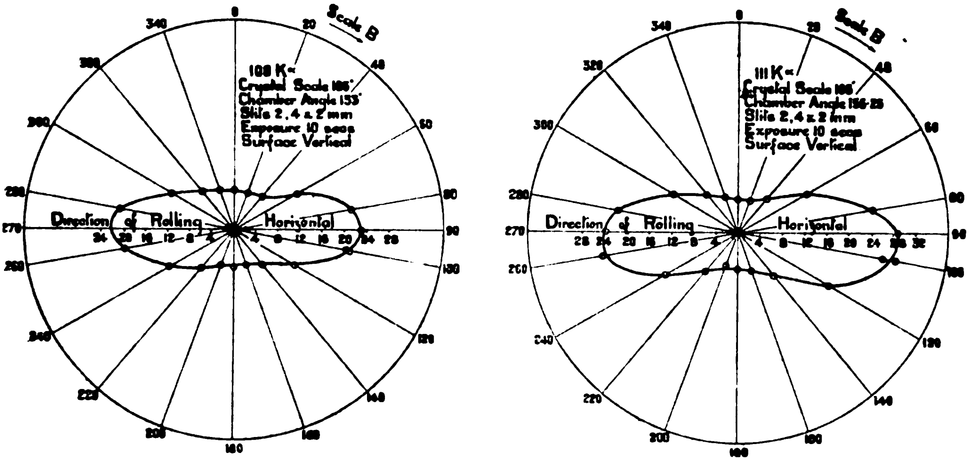
0°, 70°32′, 109°28′, 180°, 250°32′, and 289°28′,

while the observed figures are

0°, 62°, 118°, 184°, 241°, and 297°.

The separation of the first two peaks of the observed series differs from the calculated value by 8·5°, which is more than the limit of error of experiment. Several specimens were examined, and great care was taken in each case to get the planes in the best reflecting position by rotation about the axes A and B (Fig. 7), but the angular separation of the peaks was persistently less than 70°. The following are the figures obtained from several different samples of material: 62°, 63°, 62°, 62°, 59°; the last two figures being obtained with the rays confined by a circular aperture of 3 mm. diameter placed near the crystal slit and situated 9 cms. from the bulb slit, the rays in the first case passing through the centre, and in the second case near to the edge of the material. The observations themselves are liable to an error of about ±2°, so that there is no doubt the angle between these peaks is not greater than 65°.

It was observed from the curves which established this fact that the peak given by reflection from the (111) plane perpendicular to the plane of rolling was always about twice as wide as the peaks from the other (111) planes. This is shown in Fig. 5*a* and Fig. 10*b*. The width of the peak being taken at half its height, we have for the widths of the peaks in Fig. 5*a*, starting from the left,



(*a*) FIG. 9. (*b*)

11°, 23°, 11°, 14°, 23° and 10°,

and in Fig. 8*b*, 12°, 20° and 10°.

The central peaks are due to the reflections from planes whose traces on Fig. 8 are the lines *OB* and *OB'*. Calculations shows that a (311) plane belonging to the same zone cuts the plane of Fig. 8 in the line OA_1, inclined at 10° to *OA*, and its reflection in the plane of the specimen is the line OA_1', the former belonging to the set of crystals "*a*" and the second to the set "*b*," which is the reflection of "*a*" in *OA*. Since the reflection from (311) is particularly intense in the surface of the sheet, let us suppose that the set "*a*" deviates from the ideal position considered above by 10°, so as to bring its (311) plane into the surface, and that the set "*b*" also deviates by 10° in the opposite direction. The areas in which the various planes will be localised are shaded horizontally for the "*a*" set and vertically for the "*b*" set in Fig. 8, and it will be seen that the planes whose mean position is *BOB'* diverge 10° on either side of that line, while for the other lines, such as *OC*, the divergence is in one direction only. For *OC* it is towards *OB*, and for *OC'* away from *OB*, which is precisely the effect observed in the measured angular distances between these peaks, the *OC* peak occurring 8° too close to *OB* and the *OC′* peak 9° too far from *OB*.

Assuming now that the observed peaks represent the centres of the shaded areas of Fig. 8, the following table shows the agreement between the positions of the observed peaks and the positions in which they would be expected from Fig. 8.

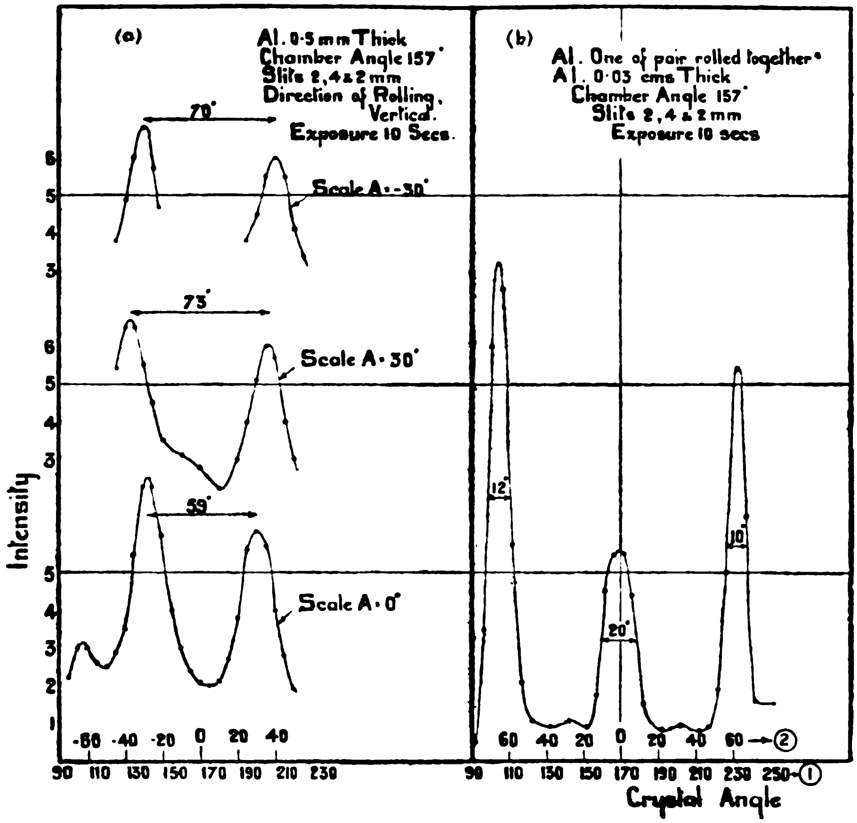


Fig. 10.

Calculated.	Observed.		
Fig. 8.	Fig. 5*a*.	Fig. 10*b*.	Another specimen.
0	0	0	0
65	62	63	63
115	118	(115)*	116
180	185	(180)*	(180)*
245	240	(243)*	(243)*
295	294	295	295

* The figures in brackets are inferred from those observed by the addition of 180°.

Fig. 6 is analogous to Fig. 5*a*, but in the former the ionisation chamber was set to receive the rays reflected from the (100) (Fig. 6*a*) and (110) (Fig. 6*b*) planes. In comparing the positions of the planes as observed with those to be expected from the scheme illustrated in Fig. 8, we have to start from the same scale reading (166°) as for the (111) planes, and add to the figure so found the difference between the angles of reflection for (111) and those for the planes considered. We have

$$\theta_{111}=8{\cdot}7^\circ,\ \theta_{100}=10{\cdot}1^\circ \text{ and } \theta_{110}=14{\cdot}4^\circ.$$

So to the observed figures, starting from 166° as zero, we must add 1·4° for the (100) and 5·7° for the (110) planes, or to the limits of accuracy required 1° and 6° respectively. The following table shows the results of the comparison of the observed (100) reflections with those expected :—

Observed (Fig. 6*a*).	Observed + 1°.	Calculated.
0°	1°	(111$K\alpha$)
32°	33°	(220$K\beta$)
59°	60°	60°
120°	121°	120°
150°	151°	(220$K\beta$)
185°	186°	(111$K\alpha$)
212°	213°	(220$K\beta$)
240°	241°	240°
300°	301°	300°
328°	329°	(220$K\beta$)

The suggested arrangement evidently accounts satisfactorily for the four larger peaks of Fig. 6*a*. The small peaks at 0° and 185° are undoubtedly due to stray reflections from the (111) planes which occur at these angles (Fig. 5*a*). So we are left with peaks at angles of 33° and 151° with *OB* to be accounted for, the intensity of these being but one-tenth of that of the other four. The larger peaks are represented in Fig. 8 by the lines *OD* and *OD′*, and are situated at the middle of the shaded areas shown in that diagram.

Turning now to the (110) planes (Fig. 6*b*), we have the following comparison between the observed and calculated angles :—

Observed (Fig. 6*b*).	Observed + 6°.	Calculated.
23°	29°	30°
(85°)	(91°)	...
(115°)	(121°)	...
(147°)	(153°)	150°
(203°)	(209°)	210°
265°	271°	...
295°	301°	...
327°	333°	330°

Again we are left with two peaks unexplained at angles of 91° and 121° with *OB*. The remaining planes are represented by the lines *OE* and *OE′* in Fig. 8, and the agreement between the suggested arrangement and the observed position of the planes is again good.

We notice that (110) planes occur at angles of 29° and 333°, which are very close to the two unexplained peaks at angles of 33° and 329° in Fig. 5*a*. The angle of reflection from (100) planes for $K\alpha$ radiation is 10·1°, and from (110) planes for $K\beta$ is 12·7°, the difference 2·6° being comparable with the angular divergence of the incident beam of X-rays. It would, therefore, be possible for $K\beta$ radiation reflected from (110) planes to enter the chamber slit even when that was set to receive $K\alpha$ radiation reflected from (100) planes. The point was tested by placing a zirconia filter in front of the ionisation chamber, and the result is shown in the upper curve of Fig. 6*a*. The third peak is quite distinct, but the second and fourth have disappeared, there being no variations in the region where they were expected that cannot be ascribed to experimental error. All the maxima of Fig. 6*a* have now been accounted for, and we have now to explain the presence of the peaks at angles of 91° and 121° in Fig. 6*b*, when the chamber was in the position to receive the (110) reflections.

It appeared possible that part of these two peaks might be due to scattered radiation, since the minima in Fig. 6*b* occur at points where the metal plate is parallel to the incident and reflected beams respectively. The upper curve in Fig. 6*b* shows the effect obtained when a plate of glass 2 mm. thick was substituted for the metal plate on the spectrometer table. Minima are observed in the places where the absorption is evidently greatest,.and maxima occur sensibly at the same angles as for the metal plates. The second and smaller unexplained peak is probably entirely due to this effect. The first must be partly due to the same effect, partly due to $K\beta$ radiation reflected from (311) planes parallel to the surface, and partly due to reflection of $K\alpha$ radiation from the (110) planes, which with the suggested crystal orientation are inclined at 30° to the vertical (specrometer axis), and no doubt deviate from this ideal position to some extent.

Further experiments were carried out on the reflections from (100) and (111) planes with a view to ascertaining the effect of scattering. In the case of (100), for example, the crystal table was rotated until the (100) plane giving the first peak on the left in Fig. 6*a* was in the position to reflect the $K\alpha$ radiation, the chamber being situated in the proper position (reading on scale of chamber 153°) to receive the (100) reflection. The specimen was rotated in its own plane and readings taken at intervals of 20° (10° near the maxima) on the B scale. The results are shown in Fig. 9*a*. It will be observed that two maxima appear, separated by 180° in accordance with the arrangement of planes shown in Fig. 8, and that the intensity of these maxima is about three times that of the radiation scattered into the chamber when the specimen is in the other positions. Similar effects are shown in Fig. 9*b* when the reflections from (111) planes were examined.

The specimen used to obtain the curve in Fig. 5*a* (0·5 mm. thick) was rotated in its own plane until the direction of rolling was vertical. The ionisation chamber was set to receive (111) reflections and the crystal table rotated, the readings being taken at 5° intervals as for the curve in Fig. 5*a*. The result is shown in Fig. 10*a*. Reflections from (111) planes occur at angles $-29°$ and $+30°$ from a vertical plane perpendicular to the surface of the material. There is very little trace, if any, of (111) reflections from planes perpendicular to the surface.

The observed reflections agree with those to be expected from the arrangements suggested in the present Paper, according to which we are in the above experiment rotating the cube about the cube diagonal. The (111) planes are then inclined at 20° to the axis of the spectrometer, and will come into the reflecting position at 60° intervals, which is within 1° of the figure observed.

The specimen was now rotated about the axis A (Fig. 7) until the direction of rolling was 30° to the vertical. The peaks separated to 73°, and at $-30°$ to the vertical the value of 70° was obtained as shown in Fig. 10*a*. These observations again agree with the reflections to be expected from the crystal orientation suggested here. The theoretical separation of 70°32′ is obtained because the planes at which reflections occur belong to the same set of crystals (either set " *a* " or set " *b* ").

This experiment shows that the arrangement of crystals suggested by Mark and Weissenberg does not exist to any appreciable extent in aluminium rolled from 1 cm. to 0·05 cm. thickness.

The above results, which were exclusively obtained with the ionisation spectrometer, confirm the conclusions of Wever.

II. MEASUREMENTS BY THE PHOTOGRAPHIC METHOD.

It was considered advisable to examine the problem further by the photographic method, in view of the discordant results obtained by previous observers with this method of analysis. The rotating crystal method was used, the specimen of foil 0·01 cm. thick being rotated during exposure about the direction of rolling, the transverse direction and the foil normal respectively. The three photographs so obtained are shown in Figs. 11, 12 and 13, radiation from a copper anticathode being employed in each case. If we take a line on the photograph perpendicular to the axis of rotation, and call the angle between this line and the line joining one of the diffraction spots to the centre spot α, then

$$\sin \alpha = \frac{\cos \varphi}{\cos \theta}$$

where φ is the angle between the axis of rotation and the normal to the plane giving the spot, and θ is the glancing angle of the X-rays. It is, therefore, possible to calculate the values required by the arrangements of Mark and Weissenberg, and by that of Wever. This has been done, and the results are shown graphically for comparison with the photographs.

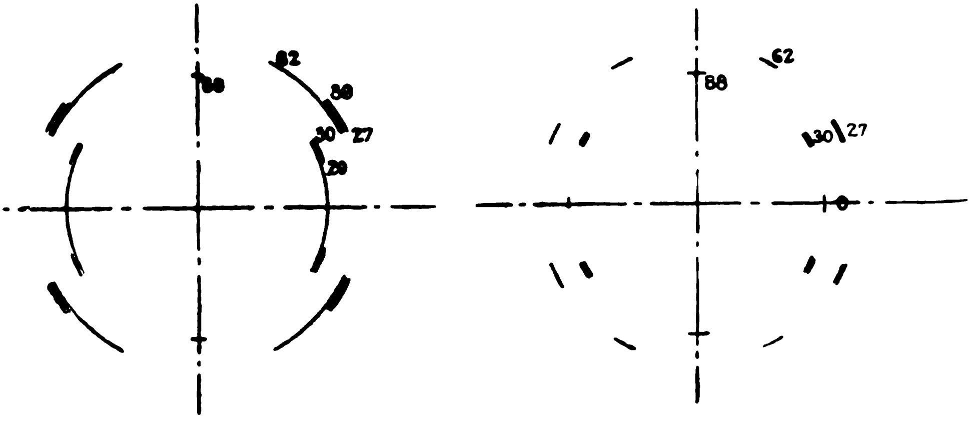
In Fig. 11 we have a photograph taken with the specimen rotating about the direction of rolling. The type of picture to be expected if the axis of rotation is within 8° of a [112] direction is shown in Fig. 14*a*, while Fig. 14*b* is constructed on the assumption that the axis lies anywhere between [111] and [112]. The chief difference between the two calculated diagrams is that in the latter the spots tend to run together. On the photographic plate the reflections of 100 planes seem to be a continuous band from $\alpha=26°$ to $\alpha=64°$, with a very intense spot in the region covered by the smaller values of α. The photograph can be equally well interpreted by either arrangement.

Fig. 12 is a photograph taken during rotation of the specimen about the transverse direction. Fig. 15*a* is calculated from Mark and Weissenberg's data, the axis of rotation lying between [201], [111] and [021]. Fig. 15*b* is constructed for the case when the axis lies between [110] and [221]. The position of the reflections from (100) is in agreement with the latter arrangement.

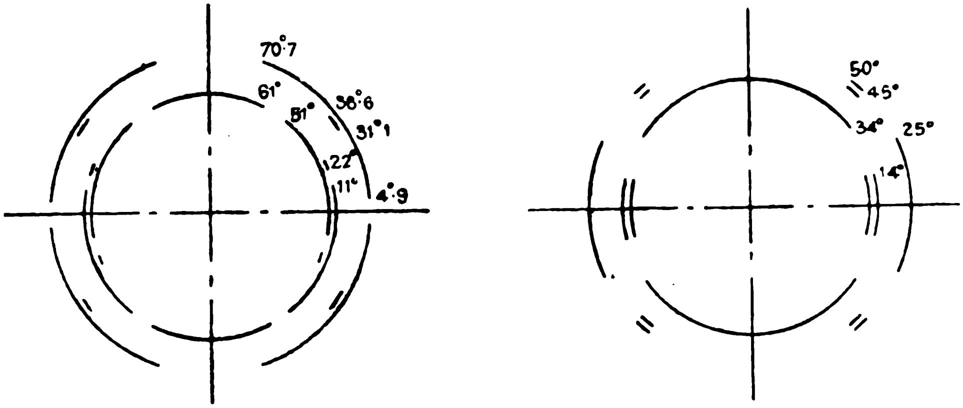
The former requires this spot to lie in a position for which $\alpha=35\pm4°$, the latter requires $\alpha=47\pm3$, while the observed value is 46 ± 10, the greater width being due to the divergence of the X-ray beam. The arrangement of Mark and Weissenberg does not explain the position of the spots on this photograph.

The photograph in Fig. 13 is taken with the specimen rotating about the foil normal. It may be compared with Fig. 14*a*, which shows the theoretical distribution for rotation about a [112) direction.

The photographs agree with the results obtained with the spectrometer, and confirm the results of Wever.



(*b*) FIG. 14. (*a*)



(*a*) FIG. 15. (*b*)

CONCLUSIONS.

When a cast specimen of aluminium containing a number of comparatively large crystals orientated at random throughout the body of the material is rolled, the crystals break up into a large number of minute crystals. As the thickness of the material is progressively diminished, the small crystals tend to take up a definite orientation, each crystal having a cube diagonal in the direction of rolling and a (211) plane in the plane of rolling.

Two sets of crystals exist in the material after rolling, the one set being the optical image of the other in the plane of rolling.

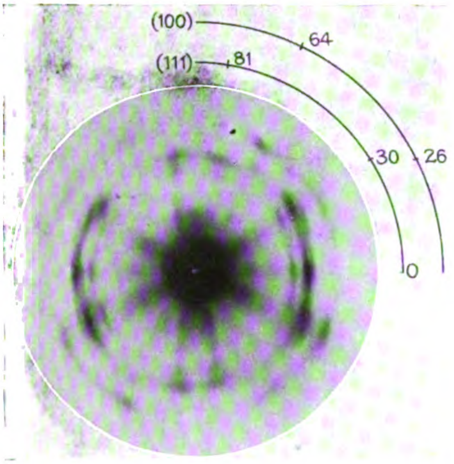


FIG. 11.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL TAKEN DURING ROTATION OF SPECIMEN ABOUT THE DIRECTION OF ROLLING.

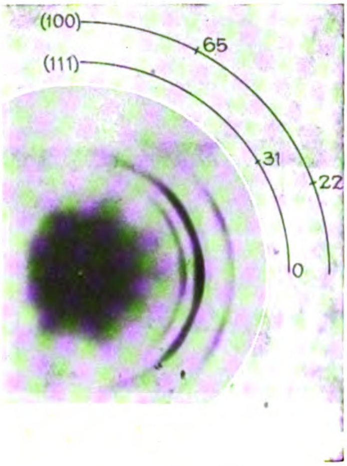


FIG. 13.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL TAKEN DURING ROTATION OF SPECIMEN ABOUT THE FOIL NORMAL.

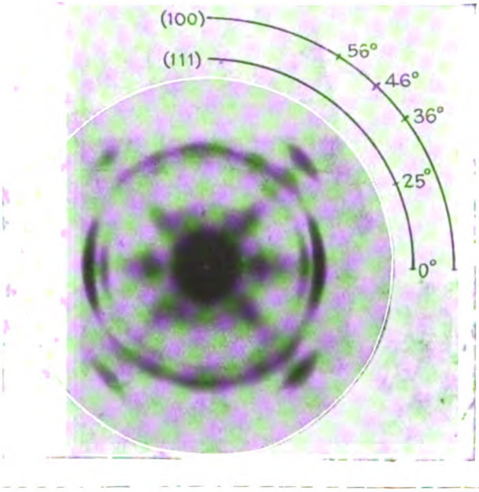


FIG. 12.—X-RAY PHOTOGRAPH OF ALUMINIUM FOIL TAKEN DURING ROTATION OF SPECIMEN ABOUT THE TRANSVERSE DIRECTION.

To face page 146]

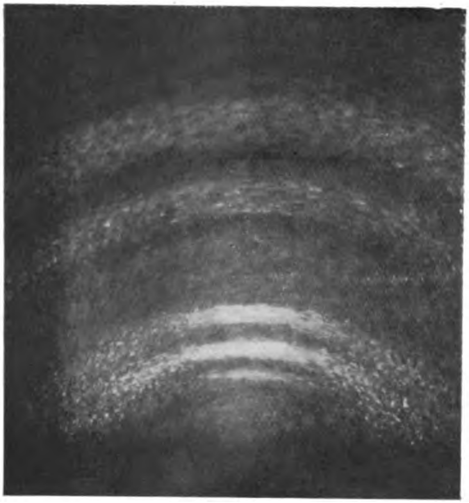


Fig. I (*Discussion*).

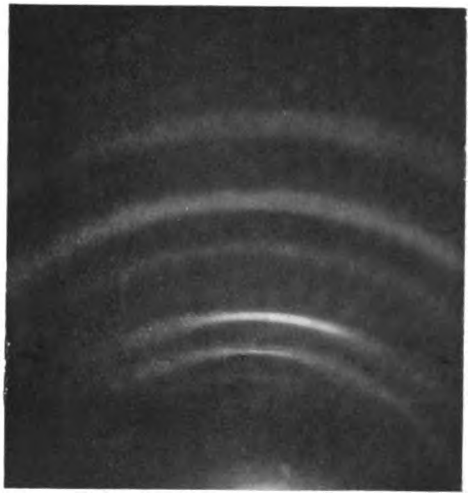


Fig. II (*Discussion*).

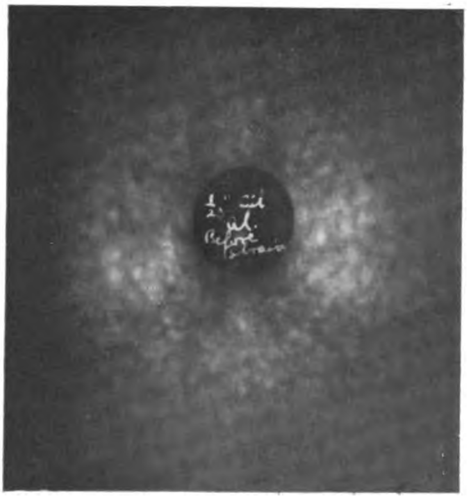


Fig. III (*Discussion*).

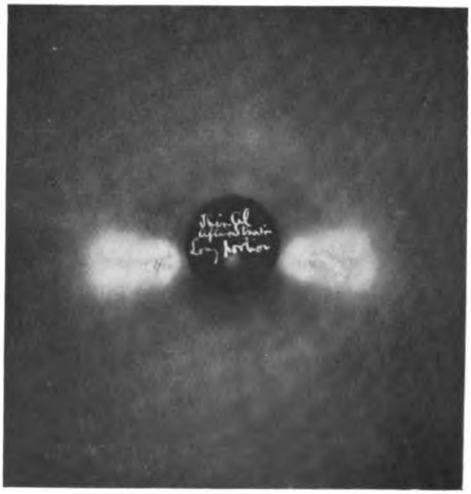


Fig. IV (*Discussion*).

[*To face page* **147**

The observations obtained by the ionisation spectrometer indicate that the type of the space lattice remains unaltered, and that the parameter of the material in the severely worked condition does not differ from that of the annealed material by more than 0·5 per cent. On the other hand, the diffraction spots on the photographs are rather broad. This would suggest either that the parameter is subject to variations—in other words, that the lattice is distorted—or else that the crystals are of colloidal dimensions. The experiments described above are probably in themselves insufficient to decide between these two alternatives. It is to be observed, however, that deformation which takes place by "slip" produces subdivison of the crystals, and may or may not be accompanied by linear deformations. Determinations of the density of the material as cast and in various conditions after rolling showed no variations greater than 1 part in 1,000. This indicates that the average lattice constant does not on the whole differ from the normal by more than 1 part in 3,000, and lends support to the determination by means of the spectrometer. It does not, however, dispose of the possibility of the material being self-strained in such a manner that parts of it are compressed while others are extended.

DISCUSSION.

Miss L. **Elam** discussed the relative merits of the photographic and the ionisation-spectrometer methods. The latter method she considered somewhat unreliable for the present purpose, unless elaborate precautions be taken to move the specimen about both vertical and horizontal axes. If the reflecting planes be not accurately vertical, reflexions may occur which fail to enter the chamber and so pass unnoticed, and in any case the intensity is so much affected by the inclination of the specimen that little importance can be attached to the maximum and minimum values obtained. Thus the flattening of the peaks in Fig. 3 may be due to this cause, the orientation of the crystals being altered in the vertical plane by rolling ; some of them may become placed in a more favourable position for affecting the chamber. This suggestion is borne out by the photographs in the Paper, since they show an almost continuous ring of scattered radiation where the ionisation chamber gives indications corresponding to only a few degrees of this ring.

Prof. F. L. **Hopwood** said that both speakers had avoided referring to the amorphous surface layer. Had the assumption that such a layer exists been abandoned ?

Dr. E. A. **Owen**, in reply, said that he disagreed with Miss Elam. He considered that the spectrometer method was as reliable as, if not in some respects superior to, the photographic method. In the latter the photographs showed reflections from a number of crystal planes in the specimen, but they gave no indication as to the orientation of the specimen when the reflections occurred. In the spectrometer method, as used here, the specimen could be turned in any direction so that the reflections from any desired set of planes in the specimen could be examined. He was of opinion, however, that the most satisfactory procedure was to employ the two methods in conjunction, as had been done in the investigation described in the Paper, in which an attempt was made to decide between two discordant results obtained by the photographic method. No indication of an amorphous layer had been found in these experiments.

Dr. E. V. **Pullin** (communicated) : It may be of interest if I contribute one or two spectrograms which serve to illustrate Dr. Owen's remarks. These were obtained some five or six months ago in my laboratory by Dr. Gilbert West. Fig. I is a spectrogram of aluminium before strain taken by the reflection method and using rhodium radiation. Fig. II is a similar spectrogram taken after the aluminium had been strained. It will be seen that the speckled appearance, indicating large crystals, has disappeared in Fig. II. Figs. III and IV are spectrograms taken by the transmission method using unfiltered Tungsten radiation. In Fig. III large crystals are again indicated by the spotted appearance. In Fig. IV this has disappeared, indicating once more the break-up of the large crystals into smaller ones. The figure also illustrates that although broken up, the lattices of the crystal fragments are preferentially oriented.

XVIII.—THE SPREADING OF ONE LIQUID ON THE SURFACE OF ANOTHER.

By R. S. Burdon, *B.Sc.*, *A.Inst.P.*, Lecturer in Physics, University of Adelaide.

Received October 30, 1925.

(*Communicated by* Mr. Edwin Edser, A.R.C.S., F.Inst.P.)

Summary.

The Paper gives an account of preliminary investigations into the spreading of liquids on mercury. Water and solutions of a number of inorganic substances are tested.

Purest "conductivity" water in the presence of air is found to spread very slowly on a clean mercury surface; the spreading is greatly accelerated by traces of acid in solution, and totally inhibited by traces of alkali.

All the neutral salts tested, even chlorides of mercury and silver, are found to produce rapid spreading. By varying the concentration of the solution the rate of spreading is controlled; the phenomena are described and photographed.

All acid solutions tested spread rapidly, probably reacting chemically with the mercury. One part of hydrochloric acid in ten million of water definitely accelerates spreading. A drop of very dilute acid spreads rapidly to cover a definite area and stops, any further spreading being as slow as that of water. The area covered during the rapid stage depends on the nature of the acid; it is proportional to the number of acid molecules present, and is larger than would be expected if a monomolecular layer of the appropriate salt were formed on the mercury surface.

Drops of certain alkaline solutions, notably ammonia, are found to spread after a period of delay, the spreading being due to carbon dioxide absorbed from the air.

Electrostatic fields up to 4,000 volts/cm. applied perpendicular to the surface produce no visible results. Placing a platinum wire from one terminal of a battery in the mercury and from the other terminal in the drop, and applying small voltages, causes spreading even in alkalis if the mercury be positive, and prevents spreading even in dilute acids if the mercury be negative.

Increasing the field beyond that necessary to prevent spreading (mercury negative) sets up an oscillation, the drop spreading till it breaks contact with the terminal, and then contracting. An E.M.F. of 400 volts was required to produce this effect with a drop of conductivity water.

A method of photographing films on the surface of mercury is described. By the same means a photograph is obtained showing a drop of oil spreading on a water surface. The spreading film is preceded by a well defined ridge, probably that observed by Osborne Reynolds, but apparently by none of the more recent writers.

The Paper concludes with a description of a ridge that may be observed under certain conditions when water is draining from a sheet of perfectly clean glass.

I. Introduction.

In recent years a number of investigations by different inquirers have dealt with the spreading of organic liquids on the surface of water, and particularly with the nature of the molecular surface film in its condition of extreme tenuity.* The corresponding phenomena when mercury is substituted for water have not received an equal amount of attention. With a view to ascertaining what specific differences might exist in the case of the two liquids, and particularly in order to test the correctness of the view regarding the part played by chemical affinity in the phenomena of spreading, the investigation hereunder described was proposed to me by Prof. Kerr Grant in 1922, and has been proceeding since that date.

---

* Langmuir, Jour. Am. Chem. Soc., September (1917). Harkins, Jour. Am. Chem. Soc., p. 354 (1917). Adam, Proc. Roy. Soc., A. 99, p. 336; and A. 101, p. 452. Labrouste, Ann. de Physique, 14, p. 164.

The Paper contains an account, which is almost purely descriptive, of the more important results which have been obtained. No comprehensive theory has yet been found to cover all the observed facts, which appear to be as difficult to explain on the basis of Langmuir's chemical theory of spreading as on that of the customary physical theory.

II. PREPARATION OF MATERIALS.

The difficulty of obtaining a perfectly clean mercury surface can only be realized by those who have attempted to work with this liquid on surface tension phenomena. No ordinary "chemically pure" distilled mercury is of the slightest use. After trying several of the usual methods of cleaning mercury without success, it was found that by distilling in a hard glass still in a slow air current, and then shaking thoroughly with a mixture of sulphuric acid and potassium bichromate, it was possible to obtain mercury having a satisfactory surface.

This method gave mercury which henceforth, so long as it received no fatty contamination, only required to be washed and passed through a separating funnel in order to give consistent behaviour.

Mercury is exceedingly liable to receive contamination from glassware. In some of the experiments glass dishes 3 in. in diameter and ¼ in. deep were used. Three of these were washed in strong chromic acid solution for some hours, then boiled for some time in distilled water and rinsed in pure cold water. They maintained a perfect unbroken water film until dry, yet when filled with clean mercury from the same bottle they showed distinct characteristics; a drop of tap water placed on mercury in the first dish spread completely; there was only a slight spread on mercury in the second dish, and none at all in the third.

Prolonged treatment finally brought the dishes to a uniformly satisfactory state, after which they remained clean if reasonable care were exercised.

III. WATER ON THE SURFACE OF MERCURY.

There are still differences of opinion as to the behaviour of pure water on a mercury surface. The observations of Harkins* agree in a general way with those made in these experiments.

In the presence of air, a drop of ordinary distilled water placed on a fresh mercury surface spreads slowly and uniformly, retaining its circular form. The spreading continues until, under the processes combined with evaporation, the drop passes through a stage showing film-colours, and vanishes by evaporation. (This forms a simple test of the perfection of the mercury surface.) If this has not involved too long an exposure of the mercury surface, a second drop will behave in a similar manner. Harkins* states that a mercury surface exposed to air rapidly becomes contaminated by a film of water-vapour, and suggests this as the reason for water not spreading on a surface which has been exposed for any length of time. It is found, however, that a drop of water will spread on the surface after a previous drop has spread and evaporated, and also after the mercury has been exposed in an atmosphere saturated with water-vapour until a visible film has condensed on it, and the surface is then allowed to dry without disturbance. In the presence of a saturated atmosphere, however, a drop of water does not spread. Moreover, if the mercury surface be contaminated by the addition of one-tenth the amount of oil necessary to give a monomolecular layer over it, the water is prevented from spreading.

---

* Journal Am. Chem. Soc., December (1920), and December (1922).

A drop of tap-water spreads many times faster than distilled water. The purer the water the more slowly it spreads. High-grade conductivity water was prepared by re-distilling conductivity water in a pyrex all-glass still and condenser. This water is found to spread uniformly taking possibly 5 minutes for a drop to spread to a disc 5 cm. in diameter. Water from a soft glass still did not spread, and this was found to be due to traces of alkali present even after steaming out for some days. (*See* Section VI.)

In an atmosphere containing a high percentage of CO_2 a drop of conductivity water spreads rapidly after a few seconds. A small percentage of NH_3 in the atmosphere entirely prevents spreading.

The increasing slowness of spread with increasing purity of water makes it at least probable that pure water spreads on the surface of mercury only in virtue of the presence of dissociated molecules. Evidence given later shows that the presence of the H-ion accelerates spreading while the OH-ion retards or inhibits it.

IV. SOLUTIONS OF INORGANIC SALTS.

The addition of acid or neutral salt to water greatly increases its rate of spreading on mercury. One part NaCl in 100,000 parts water markedly increases the rate and the effect of one part HCl in ten millions of water is quite evident.

If the spreading is not too rapid, and the mercury is in perfect condition and free from vibration, the drop maintains a circular form having a ridge around the periphery. This ridge then develops irregularities which slowly resolve themselves into droplets. The phenomenon appears to be of the same nature as that observed by Devaux* when benzine spreads on slightly contaminated water, but here the process can be made to take place quite slowly and the changes studied in detail.

The very general occurrence of this ridge at the edge of the spreading liquid appears to support the theory of squeezing action as the cause of spreading.† This is particularly the case with very dilute HCl in which one would expect the active cause of spread (HCl) to be less concentrated at the advancing periphery of the drop than elsewhere owing to its removal by reaction with the mercury. (*See* Section V.) The centre of the spreading disc where the HCl is more concentrated might then exert a squeezing action forcing the liquid to spread outward as indicated by the ridge. The difficulty here as in other cases is to picture the mechanism by which the addition of one molecule of HCl to some millions of water-molecules is going to greatly increase the squeezing action between the water and mercury.

Photography of water films possibly less than one thousandth of an inch in thickness on a mercury surface presents difficulties, but by the method described in Section VIII, the accompanying plates (Nos. 1-10) were obtained. These give an idea of the phenomena occurring during spreading, but each picture represents a different drop as it was not possible to obtain a series showing the stages from a single drop. Moreover the pictures are foreshortened, circular drops appearing

---

* Jour. de Physique, p. 698 (1912).

† Edser: Fourth Report on Colloid Chemistry, B.A.A.S.

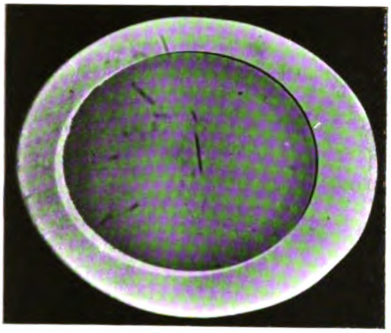


PLATE 1.

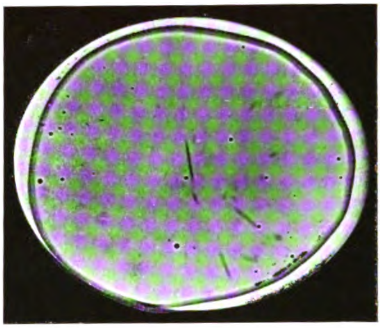


PLATE 2.

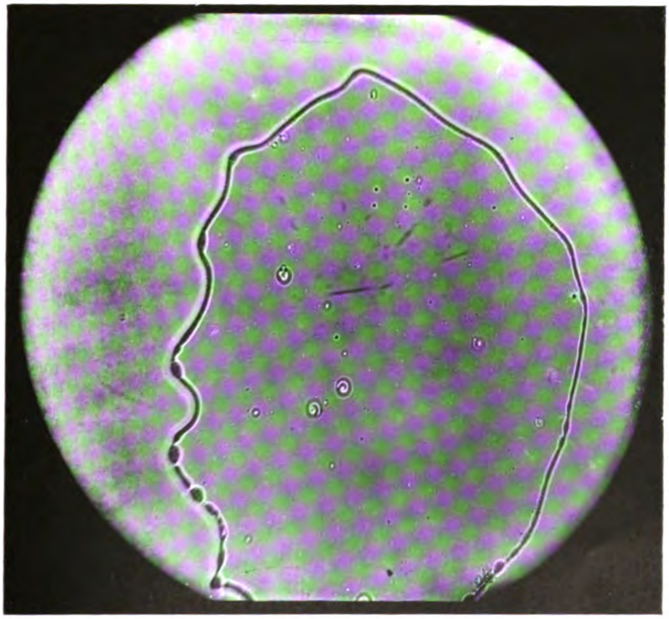


PLATE 3.

[*To face page* **151**]

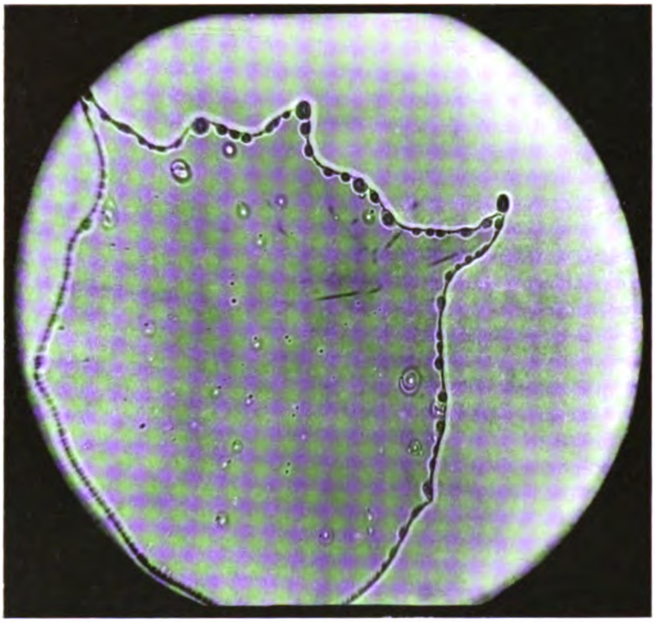


PLATE 4.

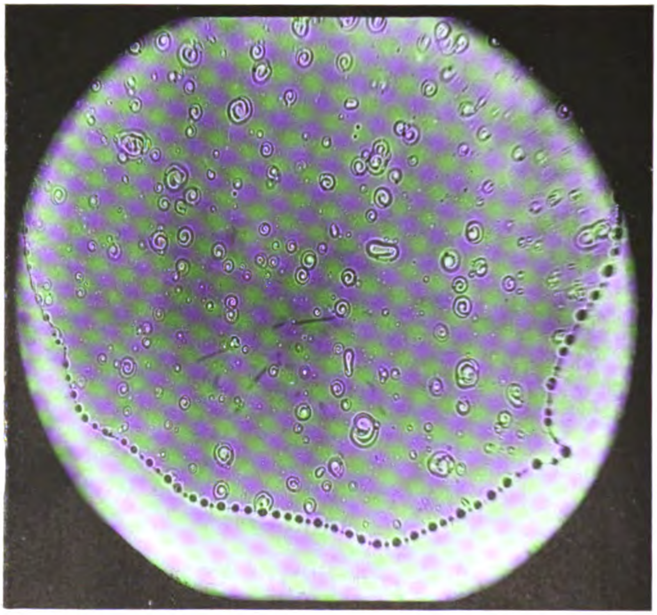


PLATE 5.

[*To face page* **151**

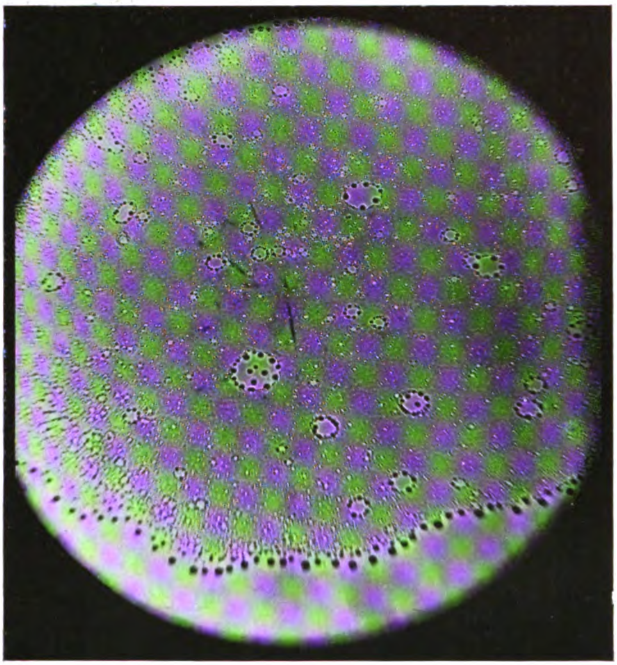


Plate 6.

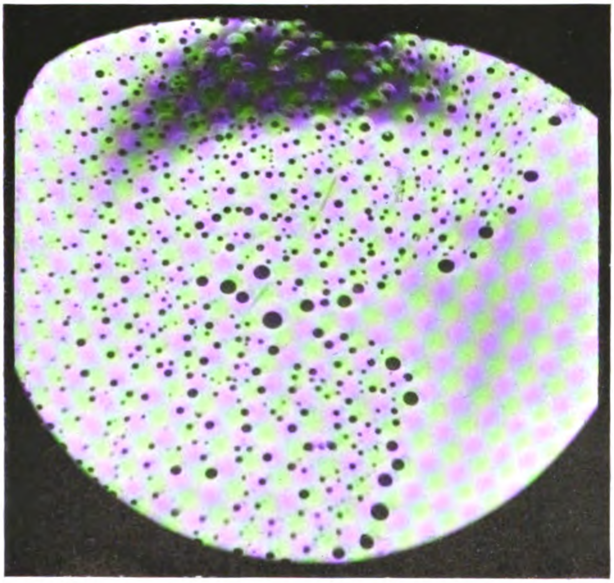


Plate 7.

[*To face page* 151]

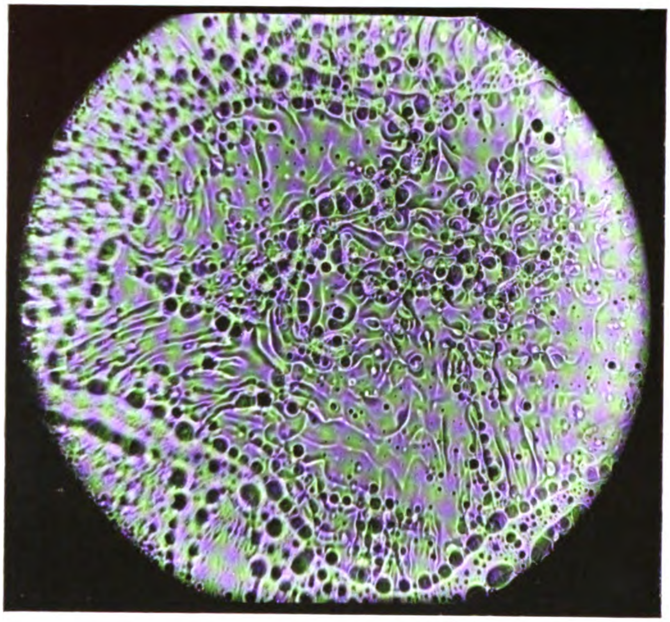


PLATE 8.

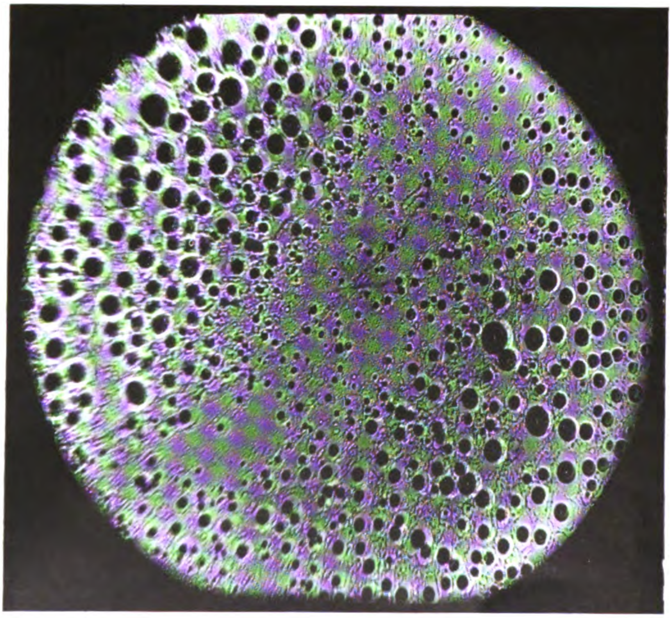


PLATE 9.

[*To face page* **151**

as ellipses. The amount of foreshortening is shown by Plate No. 1, which represents a drop of conductivity water that has spread to a circle 3·5 cm. in diameter.

All the plates show certain markings near the centre which are due to flaws in the large lens of the optical system being reflected in the mercury surface.

Plates Nos. 2-7 represent drops of 0·05 normal solution of NaCl. The peripheral ridge is shown (Nos. 2-4), the development of instabilities in this ridge finally giving a surrounding ring of droplets (Nos. 4, 5 and 6). The solution then pulls away from this ring of drops as shown in No. 6. The film develops further instabilities and resolves into a series of droplets more or less evenly distributed over the surface as shown in No. 7.

In obtaining these plates the mercury surface was exposed to atmospheric dust and a curious phenomenon was observed. Each dust mote landing on the very thin liquid film commences to rotate, some at high speeds, but more usually taking one or two seconds per rotation. This forces the liquid of the film out into a spiral-shaped ridge. Plates Nos. 3, 4 and 5 show progressive stages in the formation of these spirals. No. 6 shows the final stage in which each spiral has developed into a ring of droplets.

Plates Nos. 8 and 9 show the typical appearance when a more concentrated solution is used and dust is excluded. Within the outer ring of droplets (not shown in Plates) corrugations appear all over the surface (No. 8). These rapidly resolve themselves into drops (No. 9). Then as evaporation proceeds the salt crystallizes out, minute crystals forming and dashing hither and thither before attaching themselves to the crystal pattern. Beautiful opalescent colours are seen as the layer of crystals acquires the requisite thickness.

The velocity of spread is high for concentrations greater than one part salt in 20,000 of water. Below this value the rate of spread decreases rapidly.

A solution of ammonium carbonate spreads with great speed to the edge of the mercury and immediately contracts to a drop again, film colours showing for an instant over the surface after the drop has contracted. A ring of very tiny droplets is left at the outer limit to which the drop spreads. These droplets then each spread and evaporate leaving a film of carbonate over the mercury. As soon as this process is completed the original drop flashes out again throwing off a second ring of droplets. This goes on until the whole surface is covered with a solid deposit of carbonate.

The process here appears to be of the same nature as that observed with certain oils on water, i.e., the solution spreads but becomes unstable and the surplus liquid rapidly collects into a drop again. In the case of some oils on water this condition is then stable but with the solution on mercury the process is repeated. The thin film evaporates and since the ammonium carbonate left behind apparently does not affect the surface tension of the mercury the drop of solution spreads again as soon as evaporation is complete.

By using solutions of different salts a great diversity of effects is shown. No two salts behave in quite the same way, though there are certain broad similarities, solution of salts of a given type (e.g., carbonates), showing certain features in common as distinct from those exhibited by solutions of, say, the chlorides.

A point of interest is that the addition of a minute quantity of carefully washed calomel to conductivity water causes it to spread rapidly. Dr. Cooke, of this University, to whom this fact was submitted, suggests that this may be due to hydrolysis of the dissolved Hg_2Cl_2 producing free HCl.

V. INORGANIC ACIDS.

Hydrochloric acid of concentration as great as 0·01 normal flashes out over the surface and contracts again to a drop, leaving a film of calomel on the mercury. The drop then expands and contracts in an irregular manner wherever it succeeds in sweeping aside or breaking through the calomel on the mercury surface. The movements are strongly suggestive of those occurring in living micro-organizms. When the drop finally comes to rest there is a pale blue film over the mercury surface, and generally further flakes of solid within the drop. Sufficient calomel was collected to identify it by chemical tests.

(*a*) *Definite Limit to Area of Rapid Spread.*—In working with progressively increasing dilutions of any salt or acid it is found that at a certain point the rate of spread begins to decrease much more rapidly than the concentration. The dilution at which this occurs differs widely for different substances and is much greater for acids than for salts. With acids the effect manifests itself in a very striking way. Thus a drop of very dilute HCl was found to spread to a circle 4 cm. radius in one second and thereafter to spread as slowly as pure water, taking approximately a minute to increase its diameter by a further 5 mm. The transition point is very definite; using a scale supported just above the mercury surface so as to be reflected in it, it is possible to measure to within 0·5 mm. the diameter of the disc when rapid spreading ceases.

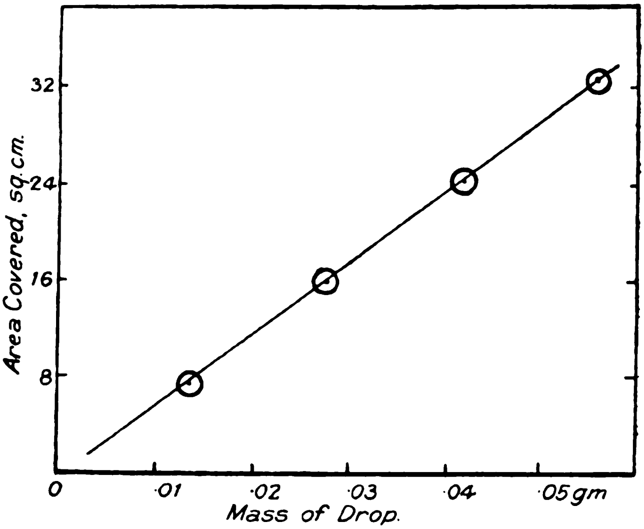


FIG. 1.—AREAS COVERED BY DROPS OF VARIOUS SIZES, USING HCl OF CONSTANT CONCENTRATION.

With a given concentration of acid the area covered during the stage of rapid spread is proportional to the mass of the drop. Fig. 1 shows mass of drop plotted against area covered for drops 1, 2 3 and 4 times the mass of the drop given by the pipette used.

With drops of constant size the area covered is proportional to the concentration. Fig. 2 shows concentrations plotted against areas covered for HCl and HBr using drops of constant size but varying concentration. Thus a drop of HCl solution spreads rapidly to an area that depends only on the number of acid molecules present in the drop. This relation certainly holds down to a point where the film is less than ·001 mm. in thickness. Always there is this rapid spreading and abrupt stoppage, followed by a further very slow spreading except in cases where the film is very thin.

Observations were taken on the areas covered by drops of known mass and concentration for HCl, HBr, and HNO_3. Solutions of moderate strength in conductivity water were prepared and measured by titration. Then by direct dilution the concentration was reduced to 0·000084 normal.

The pipette used gave drops with an average mass of 0·029 gm. Each drop thus contained approximately $2{\cdot}45 \times 10^{-9}$ gm. mol. of acid. In making the observations a reading was taken with each acid in turn and this was repeated until sufficient readings were taken. This assures that differences in area covered by different acids were not due to using mercury surfaces of varying degrees of freedom from contamination.

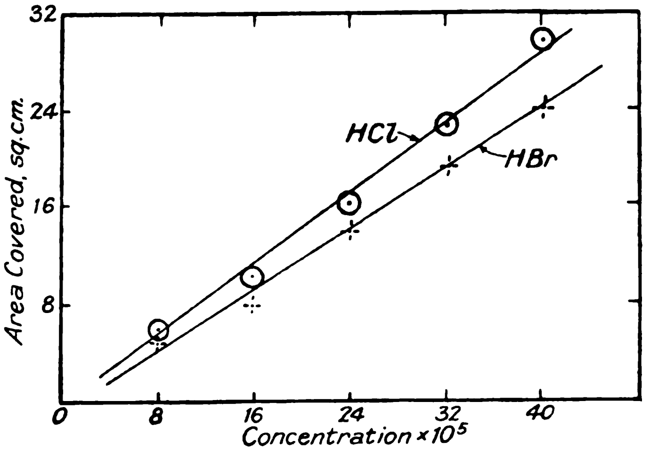


FIG. 2.—AREAS COVERED BY DROPS OF EQUAL MASS BUT VARYING CONCENTRATIONS FOR HCl AND HBr.

The mean areas covered by a drop of each kind of acid were :—

HNO_3	16·7 sq. cm.
HCl	15·0 ,, ,,
HBr	12·0 ,, ,,

Taking $6{\cdot}06 \times 10^{23}$ molecules per gm. mol. the numbers of acid molecules per sq. cm. of mercury surface when rapid spread ceased were for

HNO_3	$0{\cdot}90 \times 10^{14}$
HCl	$1{\cdot}01 \times 10^{14}$
HBr	$1{\cdot}26 \times 10^{14}$

Now 1 c.c. of mercury contains approximately

$$\frac{13{\cdot}6}{200} \times 6{\cdot}06 \times 10^{23} = 41{\cdot}2 \times 10^{21} \text{ atoms.}$$

One sq. cm. of mercury surface should, therefore, contain about

$$(41{\cdot}2\times10^{21})^{2/3}=12\times10^{14} \text{ atoms of mercury.}$$

Hence the acid spreads rapidly until it covers an area such that there is only one acid molecule to about ten mercury atoms at the common surface.

Assuming that the spreading is accompanied by chemical action here, as it certainly is at higher concentrations, it seems that only about one-tenth of the atoms in the mercury surface are attacked unless there is a transition layer of very low density at the surface of the mercury. Though the areas covered are consistent to within a few per cent., it is unlikely that a continuous monomolecular layer of mercury compound is formed on the surface, firstly, because of the large area covered per molecule of acid, and secondly, because the bromide occupies considerably smaller area per molecule than the chloride.

There does appear to be a definite connection between the area and the activity of the acid. At such dilutions there would be complete ionization, and hence identical H-ion concentrations, yet acids show these pronounced differences in the extent of spreading. Moreover, heating the mercury to 60°C. causes an increase in the area covered. The heating produces a more rapid spreading and a more pronounced peripheral ridge. After the first drop has evaporated from the hot mercury a second drop will spread. This shows that the surface is almost uncontaminated as would be expected from the small number of molecules of mercury salt formed. It is not possible, however, to repeat the process more than three or four times.

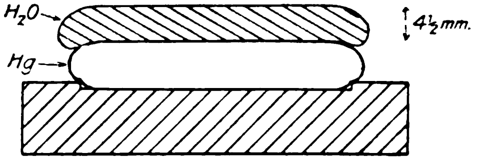


Fig. 3.—Water on the Point of Flowing over the Edge of a Mercury Surface.

(*b*) *Spreading stopped by Curvature of Mercury Surface.*—After a drop of water or solution has spread on a mercury surface it is observed that on pouring the mercury from the dish the liquid film invariably collects and travels out on the top of the mercury stream. This is the case even where a considerable amount of solution has been placed on the mercury.

By grinding a shallow depression in a sheet of plate glass and filling with mercury a surface of constant area was obtained, the surface of the mercury being well above the containing dish (*see* Fig. 3). It was found that the spreading drop never went over the curved edge of the mercury. Even with acid solution in which the velocity of spread may be a thousand times as great as that of water, the solution never goes over the edge. Using a burette, observations were taken of the amount of solution that could be added before it flowed over the edge of the mercury. Conductivity water was found to break and flow over just as the water sheet reached a thickness of 4·5 mm. Dilute acid solution ovreflowed at the same thickness as nearly as could be determined. Conductivity water was then dropped from a burette on to a freshly-paraffined glass surface and the water was found always to cover such an area that its depth was very nearly 4·5 mm. It appears then that the addition of an electrolyte to water merely increases the velocity of spread on mercury without causing it to spread further. Moreover, it is the surface tension of the solution and not that of the interface which appears to determine when the solution will flow over the curved edge of the mercury.

A small drop of olive oil or of liquid paraffin, on the other hand, at once spreads completely over the mercury surface, spreading down over the curve as readily as on the plane surface.

VI. SOLUTIONS OF INORGANIC BASES.

These solutions do not spread on mercury. Hydroxides of barium, calcium, sodium, potassium and ammonium were tested. The presence of the OH-ion tends actively to prevent spreading, i.e., it does not merely fail to cause it, for a solution of NaCl may be prevented from spreading by the addition of NaOH.

Action of Atmospheric CO_2.—A solution of pure Na_2CO_3 will not spread, but after prolonged exposure to the air it may spread owing to the absorption of CO_2. A drop of commercial ammonia fortis placed on mercury shows a violent swirling motion at the periphery, and after a few seconds begins to spread rapidly. Pure ammonia fortis was then prepared by passing NH_3 over caustic potash into conductivity water. A drop of this showed no sign of spreading or of action at the periphery for several minutes. After about five minutes the drop flattens and spreads fairly rapidly. This period of hesitation is found to be consistent and is *greater for larger drops and for more dilute solutions.* The latter fact shows that the delay is not merely the time required for the drop to lose NH_3 to the air. The spreading is due to a combination of two processes. (1) Loss of NH_3 with consequent reduction in the OH-ion concentration, and (2) the formation of $(NH_4)_2CO_3$ by absorption of CO_2 from the atmosphere. The period which elapses before spreading begins is reduced by placing the dish in a current of air containing a higher percentage of CO_2.

A solution of ammonia was prepared of such concentration that a period of seven minutes elapsed before the drop commenced to spread. Even this long period was found to be constant to within a few seconds. The extreme difficulty of maintaining a clean mercury surface probably renders this impracticable as a means of determining the CO_2 content of the air.

VII. EFFECTS OF ELECTRIC FIELDS AND ELECTROLYSIS.

Since spreading appears to be determined by the nature of the ions, it was resolved to try the effects of electric fields in controlling these.

(*a*) *Static Fields.*—One terminal of a 400-volt battery was placed in the mercury, and the other connected to a small horizontal plate which could be lowered over the mercury. For water and other liquids that do not spread rapidly, it was found that fields up to 4,000 volts/cm. produced no visible differences in the phenomena.

(*b*) *Closed Circuits.*—The effect of applying various voltages directly across the drop was then tried. One terminal was placed in the mercury and the other (a clean platinum wire) was brought into contact with the drop. With solutions of KOH or NaOH, and the mercury positive, at about 2 volts a slow spreading occurs, and a grey film (probably oxide or hydroxide of mercury) forms in concentric rings on the surface. Reversing the field causes the surface to clear, while the solution collects once more into a drop. Then, if the voltage is sufficient, the drop spreads again until it pulls away from the platinum wire. It thereupon contracts rapidly to a drop once more, comes into contact with the platinum wire and again spreads, the process repeating itself indefinitely. This alternate expansion and contraction occurs at a point that is definite to within 0·01 volt under given conditions. Just at the critical voltage the drop spreads slowly to an inch or more in diameter, and contracts rapidly on breaking from the platinum point. With a slightly higher voltage the process is so rapid that the oscillation of the drop gives an interruption of the current of sufficient frequency to cause a fluttering sound in a telephone joined in parallel with the drop. With still higher voltages (6-10 volts) the initial spread may be so violent that the drop flies to pieces.

For NaOH and KOH the oscillation sets in at a voltage close to the decomposition voltage, but the actual amount of current passing through the drop appears to be an important factor. Thus a solution of NH_4OH requires a higher voltage to produce oscillation than does a solution of KOH, although the decomposition voltage of the ammonia is the lower, the reason probably being that the ammonia has the lower conductivity. It is possible that if correction were made for voltage drop elsewhere in the circuit it would be found that oscillation begins when the decomposition voltage is applied across the solution-mercury surface.

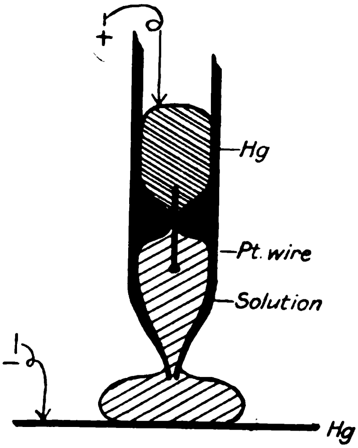


FIG. 4.—METHOD OF USING A +VE TERMINAL COMPOSED OF THE SAME LIQUID AS THAT IN THE DROP ON THE MERCURY SURFACE.

It seemed possible that the rapid oscillation of the drop might be due to an action similar to that in the Wehnelt interruptor. It is found, however, that the same effect is produced if the platinum wire is replaced by a glass tube filled with the same liquid as in the drop (see Fig. 4). The break occurs simply by the drop spreading until it pulls away from the point, and not by any film forming on the platinum. Moreover, the spreading drop is caused to contract by a break anywhere in the circuit.

It would appear that the presence of OH-ions normally tends to prevent spread, but that when they are driven on to the mercury surface by an electric field, and are able to give up their extra electron, spreading will occur. On reversing the polarity the drop progressively contracts till all the film has disappeared from the mercury. The subsequent deposition of the Na or K-ion on the mercury is accompanied by rapid spreading until the circuit is broken. Thereupon the Na or K on the mercury probably attacks the water forming hydrates which in turn cause the contraction (*see* Section VI).

The explanation, however, is not quite so simple, since this oscillation can be obtained with any solution, unless the conductivity is so high that an arc forms before the necessary voltage is reached. For a drop of conductivity water an E.M.F. of three volts is sufficient to markedly accelerate spreading (mercury positive), or to cause a partial contraction (mercury negative). A great increase in voltage, however, is necessary to make the drop oscillate, 70 volts being necessary for ordinary distilled water, and as much as 400 volts for a drop of conductivity water (in air). Apparently in this case the H-ion produces exactly the same effect as the Na or K-ion above, a much greater voltage being necessary in order to drive sufficient ions on to the mercury. The fact that a field of several thousand volts per centimetre can be applied across a drop of water without producing appreciable electrolysis is in itself interesting evidence of the quality of the water.

Substances that naturally spread rapidly were tested by holding the platinum wire just above the mercury surface (the mercury being negative) and then allowing the drop of sulution to run down the wire. Using this device, sodium chloride solution could be prevented from spreading and caused to oscillate. It was even possible to prevent dilute HCl from spreading. With a 0·0002 normal solution of HCl it requires approximately 30 volts to prevent spreading and 250 volts to produce oscillation. For higher concentrations the voltage necessary is so high that an arc forms between point and mercury surface before the value which would prevent spreading is reached.

VIII. ADDITIONAL PHENOMENA AND AN IMPROVED MEANS OF OBSERVATION.

(*a*) *Projection and Photography of Phenomena.*—Photography of thin transparent films on a perfect mercury surface is impossible by ordinary means. The modern "point-o-lite" lamp, however, gives a powerful point source, and if light from such a source is reflected by the mercury surface on to a screen a fairly well defined image of objects on the mercury surface is thrown on the screen. In particular the edges of drops and films show up owing to their curvature interfering with the regular reflection from the mercury surface. This method is of great assistance in observing phenomena, and, further, permits of their exhibition to an audience.

For photography, better definition is secured if the arrangement sketched (*see* Fig. 5) is used. Light from *P* is caused to converge on to the mercury surface *M* and is received on the photo plate after it has converged to a point and is diverging again. Definition is further improved if the lens is left in the camera *C*, and the camera focused as well as possible on to the mercury surface. The foreshortening of the picture in one direction is due to the oblique incidence of the light. This could be reduced by using more nearly normal light in the method, as used by Vincent* in his photography of ripples on a mercury surface.

---

* Phil. Mag., June (1897).

(*b*) *Ridge Described by Osborne Reynolds.*—A water surface reflects light well enough for the above method of projection to be used, when the phenomena of spreading films show up with a wealth of detail.

As is well known, if a trace of olive oil be dissolved in pure benzol, and the solution added drop by drop to a clean water surface, the first drops flash over the surface and disappear, after showing beautiful film colours. Successive drops spread more and more slowly, down to the stage where sufficient oil has been added to form a monomolecular layer on the surface of the water and drops no longer spread.

Plate No. 10 shows a drop of the solution spreading on a surface of water that has been slightly contaminated. Observation shows that the phenomena are of essentially the same nature with a perfectly clean surface, but then the processes occur too rapidly to be photographed by the method used. The limit of the visible film of benzol is clearly shown in the plate by the Newton's rings. About an inch beyond the visible drop, however, is shown a clearly defined white line, indicating sharp curvature or a ridge on the water surface. This ridge is quite invisible with ordinary methods of illumination, but is easily observed with the arrangement described. There is little doubt that this is the ridge which Osborne Reynolds observed under certain conditions when grease was spreading on a water surface, and to which Edser* refers. When a drop of the benzol solution is placed on a clean water surface the ridge travels outward so fast that it is only observed with difficulty. The principle involved in rendering the ridge visible is essentially the same as that employed by Labrouste† in rendering visible the stationary edge of a monomolecular layer of oil on a water surface.

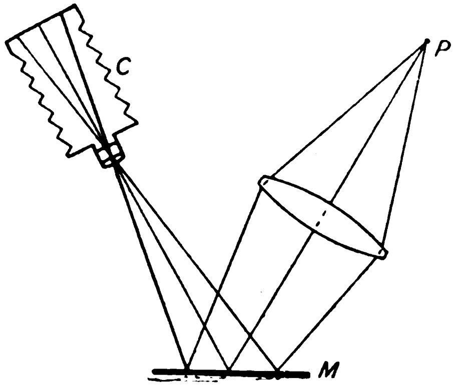


FIG. 5.—ARRANGEMENT FOR PHOTOGRAPHY OF FILMS ON A MERCURY SURFACE.

(*c*) *A Phenomenon shown by a Water Film on a Glass Surface.*—If a perfectly clean glass dish of the kind described above (Section II) be rinsed with water and then held vertically, as it drains a well defined horizontal line, apparently a ridge of water, travels *upward* across the glass. The ridge is thick enough to distort the appearance of objects viewed through the glass, and to focus sunlight shining through the dish into a sharp line of light. If, when the line has travelled half-way

---

* B.A.A.S. Fourth Report on Colloid Chemistry, p. 49.

† Ann. de Physique, 14, p. 164.

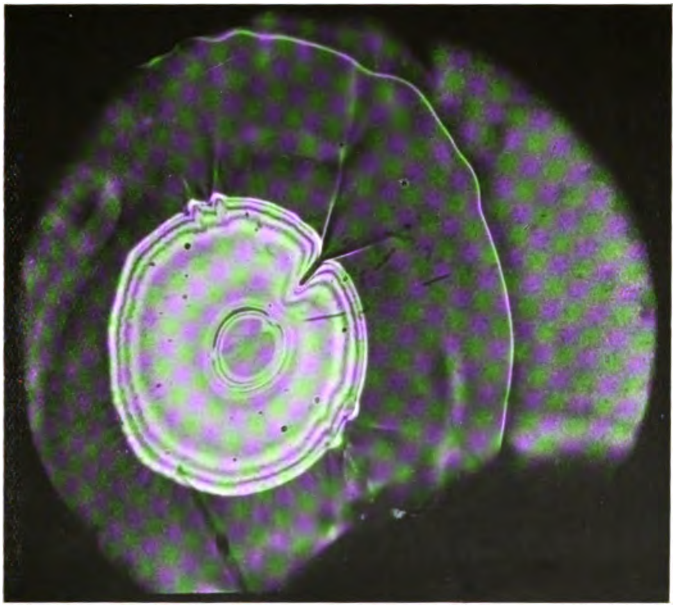


PLATE 10.

To face page 158]

across the dish, the latter be rotated through 90° making the line vertical, the lower half of the line swings round into a horizontal position and then continues to travel upward.

The same effect may be seen using a piece of plane glass, though this must be handled by means of a glass rod sealed on to the sheet in order to avoid touching the surface in lifting it from the water. Examined in sodium light, the film of water shows horizontal interference fringes which are crowded together near the ridge, indicating that it is an actual thickening in the water film.

If lycopodium be blown on to the surface after the ridge has commenced to travel across it, it will be seen that there is considerable movement in the surface layer of the film near the ridge. Some particles of the powder may be swept upward an inch or more by the ridge on its passage. Nevertheless, the water goes on draining downward throughout, and if the plate of glass is too large the ridge will fail to reach the top owing to the water film above it becoming too thin.

IX. Conclusion.

This Paper is mainly a description of phenomena observed in the preliminary work on the subject. The observations confirm the views of certain earlier writers that very minute variations decide the spreading or otherwise of water on mercury, but further show that the number and nature of ions present is an important deciding factor.

Any theory or explanation of the effects observed other than is included in general remarks in the various sections of the Paper would, at this stage, be largely guess work.

In conclusion, the writer wishes to express his thanks to Prof. Kerr Grant for helpful suggestions, encouragement and interest throughout; also to Mr. M. L. Oliphant, B.Sc., for manufacturing the stills used and for assistance both on theoretical and practical points.

DISCUSSION.

Mr. Edwin Edser read an extract from a communication from Osborne Reynolds to the British Association in 1881, describing the rib or slight elevation formed at the advancing edge of the film formed when an oil spreads over water; Osborne Reynolds concluded from this phenomenon that the forces which produce capillary effects are not confined to attractions between contiguous molecules. Mr. Edser referred to a Paper by Leslie in the Philosophical Magazine of 1802, which gives an explanation of the rise of a liquid in a capillary tube; the rise is ascribed to an attraction exerted by the walls of the tube on the neighbouring liquid which results in this liquid being squeezed up the walls, provided that the attraction extends into the liquid to a considerable distance. Reference was next made to a similar explanation of the spreading of oil over water, given by Millikan in a small text-book on physics, entitled "Mechanics, Molecular Physics and Heat," published in 1902. The water is assumed to exert an attraction on the oil, extending into the latter to a distance much greater than a molecular diameter, with the result that the oil is squeezed out over the surface until the film of oil attains a thickness of the order of magnitude of the diameter of a molecule of oil, when the spreading virtually ceases. Mr. Edser pointed out that, from the equality of action and reaction, it follows that the oil will exert a squeezing action on the superficial layer of water immediately beneath it, with the result that the advancing edge of the oil will be preceded by a minute ridge of water which has been set in motion If drops of a solution of permanganate of potash are allowed to sink through the surface of still water, vertical-coloured trails are left behind, and, on touching the surface of the water with a needle moistened with oleic acid, the trails are bent sharply just below the surface and drawn out along the surface; this experiment demonstrates that a thin film of water is set in motion by the advancing film of oil. Some oils, such as hydrocarbons of the type C_nH_{2n+2} do not spread over water, but form lenticular drops. The shape of the upper surfaces of these drops is instructive. The curvature is uniform except near the edge of a drop, where an abrupt increase of curvature is observed, giving the appearance, described by Hardy, that the surface is " tucked in " round the edge. The only explanation that can be given of this abrupt increase of curvature is that the water exerts a considerable attraction extending some distance into the oil, with the result that a pressure is produced tending to squeeze the cil out over the water ; the tendency to spread is, however, successfully withstood by the strongly-curved surface of the oil at the edge of the drop.

Mr. A. V. Slater : Although Mr. Burdon states in concluding his Paper that any theory would be guesswork at the present stage, his Paper appears to me to afford several further proofs of already fairly well-known theories. At all events it cannot but be helpful to express such phenomena as are relevant in terms of existing theories, if only with the object of stimulating discussion.

1. The " distillation theory " of spreading is still further discountenanced by Mr. Burdon's observations that spreading of water is accelerated by traces of acid and inhibited by traces of alkali, which, of course, would not greatly affect spreading by distillation.

2. According to recent work by Rideat and co-workers (Proc. Roy. Soc.), the spreading of a fatty acid on water is due to a pull across the interface and the fatty acid spreads because it, perforce, has to spread. Now, this tension across the interface is explained by molecular attraction between the COOH groups and the water ; in Mr. Burdon's case, the attraction is between a mercury surface and mercury ions in solution. The extent of the area covered during the *rapid* stage, being proportional to the number of molecules of acid present, is in accord with this theory—the attraction across the interface being between mercury atoms in the surface and Hg ions, *plus* their complement of water of hydration, in the solution. Consequently, the film will be more than a molecule thick and should depend on the extent of hydration of the attracted ion. Any water in excess of that required to hydrate the ions will spread slowly at the rate for pure water.

3. The advancing ridge observed on spreading may be due to the frictional resistance offered by the surface.

Mr. A. de Waele (communicated) : Although unable to be present at this meeting, I have had an opportunity of perusing the advance proofs of this most interesting paper. I invariably feel that great thanks are due to investigators of surface and interface phenomena for their work, owing to the close relation of such problems to cell processes and, perhaps, although the connection may not be so immediately apparent, to molecular dynamics.

A phenomenon which has given me much food for thought, but that has never struck me as of easy demonstration until this evening, is that of the disturbance of the equilibrium thickness of the critical layer by curvature of the phase of higher surface tension. That such critical thickness is modified in the direction of a very substantial increase is evident by the following consideration. Under experimental conditions well known to paint technologists, it is possible to determine the specific absorption of liquid medium necessary to convert a finely-divided solid powder to a paste, the transition from a loose non-wetting powder to a coherent paste possessing incipient adhesion (external wetting power) being quite critical. From the ratio of volumes of solid and liquid phases in the system so obtained, with powders of reasonable uniformity of dispersion and spherical form, considerable divergences are realised from the ratios corresponding to either cubical or hexagonal piling. That the discrepancy should amount to that accounted for by an interfacial layer of liquid one or two molecules thick must certainly be anticipated, but the separating layer actually calculates to a thickness of the order of, very often, one hundred molecules or more. Now, if the right-hand term of the Dupré equation referred to by Harkins as the " spreading co-efficient " be taken as the reciprocal of the relative thickness of the critical layer for a plane surface, and we take the generally-accepted statement that oleic acid spreads to a monomolecular film on water, we find that this substance marks the lower limit of thickness for liquids which are insoluble in the water phase. Returning to the solid-liquid paste previously referred to, we find that such decidedly polar phases as, let us say, zinc oxide and linseed oil, ars in equilibrium at a thickness of oil layer corresponding to about 30 molecules.

There may be several possible explanations accounting for the discrepancy in thickness of the layer surrounding curved surfaces, all of which may be related. In the first place, we have the simple hydrostatic equation connecting free or excess energy with radius of curvature, implying a minimum of free energy at infinite radius of curvature, and considerations of the wedge theory of absorbed molecules may reasonably lead us to expect tension equilibria to differ under the two conditions cited. There would appear to have been published references to the variation of surface tension with mass, but I have been unable to trace them. In any case, it seems somewhat remarkable that this obvious point of interest should hitherto have escaped comment.

XIX.—ON THE ADVANCE OF PERIHELION OF MERCURY.

By J. T. Combridge, *M.A.*, *M.Sc.*, Imperial College of Science.

Received November 6, 1925.

(*Communicated by* Prof. S. Chapman.)

Abstract.

Attention is called to the infinite possibilities of obtaining the Einstein equation for the orbit of a planet by using Newtonian mechanics with an extended potential function. The merits of the other two " crucial phenomena " as such are discussed from this point of view. It is implied that, observational tests being equally satisfied, Einstein's theory is to be preferred on account of its extensive unity and the spontaneity of its results.

SUPPOSE that in the Einstein theory of general relativity the field is such that the fundamental quadratic form can be written

$$ds^2 = V^2 dt^2 - dl^2, \qquad \dots\dots\dots\dots \quad (1)$$

where

$$dl^2 = \sum_{i,k} a_{ik} dx_i dx_k \quad (i, k=1, 2, 3) \qquad \dots\dots \quad (2)$$

is the line-element of three-dimensional space, and V (a function of the x_i only, as are also the a_{ik}) is the velocity of light at any point of that space. Such a field is said to be static. The equations of motion of a particle moving in such a field are

$$\frac{d^2x_\mu}{ds^2} + \sum_{\alpha,\beta} \left(\{\alpha\beta, \mu\} \frac{dx_\alpha}{ds} \frac{dx_\beta}{ds} \right) = 0 \quad (\mu, \alpha, \beta=1, 2, 3, 4).$$

The equation for which $\mu=4$ reduces to

$$\frac{d}{ds}\left(V^2 \frac{dx_4}{ds} \right) = 0.$$

Putting $x_4 = t$ and integrating, we obtain

$$\frac{dt}{ds} = \frac{a}{V^2},$$

a being a constant of integration. The remaining three equations of motion can then be written

$$\frac{d^2x_i}{dt^2} = \sum_k a^{ik} \frac{\partial}{\partial x_k} (-\tfrac{1}{2}V^2) + \text{terms involving } \frac{dx_i}{dt} \quad (i, k=1, 2, 3),$$

where the a^{ik} are the contravariant components associated with the a_{ik}.

The acceleration at any point, therefore, depends partly on the velocity of the particle itself and partly on a " force function " X^i defined by

$$X^i = \sum_k a^{ik} X_k \,; \quad X_k = \frac{\partial}{\partial x_k} (-\tfrac{1}{2}V^2) \quad (i, k=1, 2, 3).$$

Thus the initial acceleration of a particle placed initially at rest in the field may be regarded as due to a field of force derived from a potential function $-\frac{1}{2}V^2$. This may be compared with Einstein's result* that, for weak gravitation and for matter moving with velocities small compared with that of light, $-\frac{1}{2}V^2$ is (to a first approximation in that case) the Newtonian gravitational potential.

This relatedness between an Einstein quadratic form and a Newtonian potential function is of great use when we wish to examine the distribution of matter giving rise to a certain quadratic form. But the consequence to which it now seems desirable to call attention is the existence of endless possibilities of "explaining" the "crucial phenomena" of Einstein's theory without appeal to that theory.

The well-known quadratic form for the field of the sun is that of Schwarzschild,

$$ds^2 = c^2\left(1-\frac{2m}{r}\right)dt^2 - \left(1-\frac{2m}{r}\right)^{-1}dr^2 - r^2d\theta^2 - r^2\sin^2\theta\, d\varphi^2 \quad . \; . \; . \quad (3)$$

where $m=\gamma M/c^2$, M being the mass of the sun, γ the constant of gravitation, and c the velocity of light in the absence of gravitation.

The differential equation giving the orbit of a planet in this field is

$$\frac{d^2u}{d\varphi^2}+u=\frac{\gamma M}{h^2}+3\frac{\gamma M}{c^2}u^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where $u=1/r$.

Denoting the right-hand side of this equation in the usual way by $P/(h^2u^2)$, where P is an attracting force per unit mass, it is clear that the rotation of the apse-line can be accounted for under Newtonian mechanics by substituting a new law of force for the usual $P=\gamma Mu^2$. From such a force P a corresponding potential Ω can be found by integration through the relation

$$P=u^2\frac{d\Omega}{du}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Now (3) is not the only form in which the field of the sun can be expressed. It has been shown explicitly† that the variable r may be replaced by any function of r. This is interpreted as equivalent to adopting a different method of measuring r. Such a substitution in no way affects the amount of rotation of the apse-line of the orbit. To every function R of r which may be substituted in (3) corresponds therefore, through (4) and (5), a potential Ω which, under Newtonian mechanics and with the appropriate mode of measurement of r, will yield the required rotation of the apse-line. All these potentials are, however, merely different representations of one and the same field, and it is not this arbitrariness which gives rise to the endless possibilities mentioned above. But in discussing these it is important to obviate the arbitrariness, and to do this we shall adopt a "canonical form" for ds^2, guided by the researches of Levi-Civita on this point.‡

This geometer has written in (1) and (2)

$$V=c(1+\Gamma), \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$a_{ik}=\delta_i^k+c_{ik} \;\; (i,\, k=1,\, 2,\, 3), \quad . \; . \; . \; . \; . \; . \quad (7)$$

---

* Ann. der Physik, 49, p. 187 (1916).

† Phil. Mag., 45, p. 726 (1923).

‡ Rend. dei Lincei, Ser. 5, 26, ii, p. 307 (1917).

where ε_i^k and U are small quantities of the first order compared with unity, and δ_i^k is equal to unity or zero according as i is or is not equal to k. Hence

$$dl^2 = d\sigma^2 + \underset{i,\,k}{\Sigma_{ik}} \theta dx_i\, dx_k,$$

where $d\sigma^2$ is the line-element of Euclidean space. He then shows that every value of U satisfying the Einstein gravitational equations for a static field is a solution of

$$\nabla^2 U = O, \qquad \dots\dots\dots\dots \qquad (8)$$

the Laplacian operator relating to $d\sigma^2$ and not to dl^2. Conversely, to every harmonic function U corresponds a possible Einstein field. Further, by a proper choice of the spatial co-ordinate system, the quadratic form corresponding to any Newtonian potential c^2U can, to our order of approximation, be written

$$ds^2 = c^2(1-2U)dt^2 - (1+2U)d\sigma^2 \qquad \dots\dots \qquad (9)$$

When the co-ordinates are chosen in this way they are referred to by Levi-Civita as canonical. We cannot do better than select our canonical co-ordinate system by the same criterion.

The form to be taken as canonical for the sun's field is, therefore, the "isotropic" form of (3)*, namely,

$$ds^2 = c^2\left(1-\frac{m}{2R}\right)^2\left(1+\frac{m}{2R}\right)^{-2} dt^2 - \left(1+\frac{m}{2R}\right)^4 d\sigma^2 \qquad \dots\dots\dots \qquad (10)$$

which may be obtained from (3) by the transformation

$$r = R\left(1+\frac{m}{2R}\right)^2 \qquad \dots\dots\dots\dots \qquad (11)$$

The corresponding equation for the orbit becomes

$$\frac{d^2u}{d\varphi^2} + u = \frac{\gamma M}{h^2} + 6\frac{\gamma^2 M^2}{c^2 h^2}u \qquad \dots\dots\dots\dots \qquad (12)$$

where now $u = 1/R$ and powers of Mu above the second have been neglected. Hence the canonical expression for P is given by

$$\frac{P}{u^2} = \gamma M + 6\frac{\gamma^2 M^2}{c^2}u \qquad \dots\dots\dots\dots \qquad (13)$$

and that for Ω is, by (5),

$$\Omega = C + \gamma M u + 3\frac{\gamma^2 M^2}{c^2}u^2 \qquad \dots\dots\dots\dots \qquad (14)$$

C being a constant of integration.

But owing to the weak nature of the sun's field and the consequent approximations which it is permissible to make, any form of Ω, which can be expressed in a convergent series of ascending powers of Mu whose second and third terms agree with (14), will yield the desired result for the rotation of the apse-line. Such a potential is given by

---

* Hill and Jeffery, Phil. Mag., 41, p. 23 (1921). It is important to notice that (10) agrees with (9) only if we neglect powers of mu above the first, whereas only powers above the second may be neglected in (12) to obtain the Einstein correction term.

$$\Omega=\frac{c^2p}{6(p+1)}\left(1+\frac{6U}{c^2p}\right)^{p+1} \quad . . . . \quad (15)$$

where

$$U=\gamma Mu. \quad . . . . \quad (16)$$

This function can be expanded in a series of the kind required provided

$$\left|\frac{6U}{c^2p}\right|<1 \quad . . . . \quad (17)$$

For $p=O$ we find

$$\underset{p\to 0}{L^t}\,\Omega=U$$

so that we revert to the ordinary Newtonian potential. This corresponds with the fact that the quadratic form (9) will not give the Einstein correction term for the motion of the planet; the exact form (10) must be used and approximations made afterwards.

The possibilities thus opened up were forcibly exemplified in a recent interesting Paper by Dr. G. Temple,* the basis of which was a relation by which mass varied with potential. On that hypothesis the ordinary Newtonian equation

$$\frac{d^2x_i}{d\tau^2}=\frac{\partial\Omega}{\partial x_i} \quad (i=1,\,2,\,3) \quad . . . . \quad (18)$$

could be used provided a " proper time " τ was employed in conjunction with

$$\Omega=\frac{c^2}{4}\,(1+kU)^{-2} \quad . . . . \quad (19)$$

k is a constant involved in the fundamental relation, and to give the required result for the planet Mercury it must be taken as $-2/c^2$.

Now it is not difficult to start with a potential Ω given by (15) and to deduce the relation between M and U which must exist in order that the equations (18) may be used with the same definition of τ. The differential equation in M and U proves integrable and the result is

$$\tfrac{1}{2}K^2(p+1)(p+2)M^2U^2=M_0^{\,2}\{KU(p+2)(1+KU)^{p+1}-(1+KU)^{p+2}+1\} \quad . \quad (20)$$

where

$$K=\frac{6}{c^2p} \quad . . . . \quad (21)$$

For $p=O$, which, as we have seen, is the Newtonian case, (20) gives $M=M_0$. For $p=-3$ (20) and (21) yield respectively

$$M^2=M_0^{\,2}(1+KU)^{-2}\,; \quad K=-2/c^2\,;$$

which is the particular case considered by Temple. In a first approximation (20) gives

$$M=M_0(1+2U/c^2)$$

which is independent of p.

---

* Proc. Phys. Soc., Vol. 37, p. 269 (1925). I regret being unable to incorporate Dr. Temple's notation here. His " U " is of the opposite sign to mine.

The description of electromagnetic phenomena on Temple's hypothesis is no argument for his particular " apparent " potential as opposed to any of the other possible ones, since it requires a different value for k from the one required for gravitation.

For the displacement of lines in the solar spectrum the general relation (20) gives the same result, in a first approximation, for all values of p, and this result is twice the Einstein shift.

For the deviation of light in passing the sun it is enough to observe that the equation of motion of the light pulse is to be obtained from the exact equation (4) by making h infinite, the resulting equation being

$$\frac{d^2u}{d\varphi^2}+u=3mu^2 \qquad \ldots \ldots \ldots \ldots \quad (22)$$

which gives the Einstein deflection of $4m/\triangle$, where $\triangle$ is the perpendicular distance from the centre of the sun to the grazing ray. The light pulse, therefore, behaves like a particle of zero mass, and its deviation is entirely due to the Einstein correction term. Any theory which accounts for the advance of perihelion of Mercury by an emendation of the Newtonian equation of motion will, therefore, account also for the deflection of light in passing the sun, since the same correcting term obtains in each case. Any value of p in the relation (20) will thus account equally well for the two phenomena.

If it were originally surprising that Einstein should succeed in explaining the outstanding discrepancy in the motion of Mercury, it must have been more surprising since that the discrepancy should be explicable in so many ways. Whitehead's theory of relativity accounted for it, and that in a generous manner, for it contained three laws of gravitation which might be adopted in the absence of an electromagnetic field. The first of these is Einstein's law ; the second yields exactly the same equations of motion ; the third can be made to do so by appropriate choice of a certain arbitrary function.* Subsequent theories have aimed rather at accounting for this particular astronomical phenomenon than at building up a consistent theory of space, time and gravitation. But that much was already accomplished under Newtonian mechanics. I am not aware that even the most ardent opponent of Einstein's theory has ever accused him of inventing the theory in order to account for the discrepancy in question. Ars est celare artem. If such a charge were true Einstein would deserve even more admiration than has hitherto been accorded to him. The latest theories do not pretend to explain the discrepancy, but yield only a fraction of the usual result, and that in the opposite direction—a consummation devoutly regarded by some, since too close agreement between theory and experience would leave no room for future discovery or for the perturbations due to other planets.

It has not been my purpose to put forward a plausible hypothesis to account either for the single phenomenon under discussion or for the other phenomena which a comprehensive theory is required to explain. Rather have I tried to indicate that the motion of perihelion of Mercury can be accounted for in a very large number of ways, of which only a few have so far been advanced, and that consequently its choice in the first place as a "crucial" phenomenon was unfortunate. Seeing how the deviation of light (in passing the sun) is bound up with it, and having regard to the state of our experimental knowledge of the vibration of atoms in a gravitational field,* it would appear that until an application of Einstein's equations can be found which depends on more than one of the ten coefficients of his fundamental quadratic form there will be little hope of discriminating between his theory and endless others which can be built up by using a single potential or, as Eddington has pleasantly put it, by "tinkering with Newton's equations."

---

* Temple, Phil. Mag., 48, p. 277 (1924). This is very different from the arbitrary function occurring in the Schwarzschild solution, for the rate of rotation of the apse-line is the same for *all* values of the latter function ; it is not necessary to assign to it a particular expression in order to obtain the correct result.

*ADDENDUM.

Since the above was written it has become known that Einstein's prediction of the spectral shift has been verified in a remarkable manner by observations of the companion of Sirius. It may, therefore, transpire in time that this once disputed and despised phenomenon is the very one of the three advanced as crucial which will be decisive as between various theories. But had the prediction been proved false the fault might have lain not in the relativistic theory but in Einstein's assumption that the period of vibration of the atom is unaffected by a gravitational field. For that reason I am loth to regard the spectral shift as a phenomenon more crucial than the others.

DISCUSSION.

Dr. Temple: A curious difficulty arises in connection with equation (12), which is quoted from the paper by Hill and Jeffery. On making $h \to \infty$ in the Schwarzschild equation (4), we obtain the equation to the curvilinear path of a light pulse (22); but on making $h \to \infty$ in equation (12), we obtain the equation to a straight line. The solution of this difficulty depends upon an important distinction between the orbital equations obtained from the line-elements due to Schwarzschild and to Hill and Jeffery. The equations of motion derived from both line-elements issue in an equation analogous to Kepler's law of the constancy of areal velocity and in an equation analogous to the Newtonian law of the constancy of the total energy (potential + kinetic). The symbols a and h denote constants of integration figuring in these equations and retaining the same numerical value no matter which line-element is made the basis of our argument. In both cases we may deduce from these two equations a third equation which determines the form of the orbit. But, whereas Schwarzschild's line-element leads to an equation involving only the constant h, the line-element of Hill and Jeffery leads to the equation

$$\frac{d^2u}{d\varphi^2}+u=\frac{m}{h^2}(2a^2-c^2)+\frac{m^2u}{2h^2}(15a^2-3c^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

which involves both of the constants a and h. (N.B.—Powers of mu higher than the second have been neglected in obtaining equation A.)

In problems of planetary motion we may introduce the approximation—

$$a \doteqdot c$$

and thus deduce from equation (A) the equation given by Hill and Jeffery and here numbered (12). But in the problem of determining the deviation of rays of light by the sun, not only must we make $h \to \infty$, but also we must let $a \to \infty$, while—

$$\frac{h}{a} \to \text{a finite constant, } \Delta,$$

subsequently to be identified with the perpendicular from the centre of the sun on to the track of the ray of light. We then obtain from equation (A) the relation—

$$\frac{d^2u}{d\varphi^2}+u=\frac{2m}{\Delta^2}+\frac{15m^2u}{2\Delta^2}$$

which agrees with equation (22) in yielding the result $4m/\Delta$ for the angular deviation in radians of the light from a distant star.

It is an interesting exercise to deduce equation (A) from the Schwarzschild equation (4) by means of the transformation (11). It may be mentioned that the labour is considerably lightened by identifying not the equations themselves but their first integrals, namely :—

$$\left(\frac{du}{d\varphi}\right)^2+u^2=\frac{2m}{h^2}c^2u+2mu^3+\frac{a^2-c^2}{h^2}\text{(Schwarzschild)}$$

and

$$\left(\frac{du}{d\varphi}\right)^2+u^2=\frac{2m}{h^2}(2a^2-c^2)u+\frac{m^2u^2}{2h^2}(15a^2-3c^2)+\frac{a^2-c^2}{h^2}\text{ (Hill and Jeffery).}$$

AUTHOR'S reply : The difficulty mentioned by Dr. Temple had presented itself to me, but I was satisfied that it was purely analytical. The Schwarzschild solution and the Hill and Jeffery solution are merely different pictures of the same field, and I realised that the invisibility of a certain feature in the second canvas was due not to bad painting but to injudicious hanging. I am grateful to Dr. Temple for so illuminating the scene that the feature in question becomes easily apparent.

The transformation (11) was quoted for transition from (3) to (10).

DEMONSTRATION OF AN INSTRUMENT FOR IMITATING THE EASTWARD DEVIATION OF BODIES FALLING FROM A GREAT HEIGHT.

By G. R. Mather.

If a body, initially stationary with respect to the earth, be allowed to drop from a height, it will appear to move eastward as it falls. Newton suggested that this phenomenon might possibly furnish a measure of the earth's rate of rotation, and a photograph of his autograph letter on this subject was shown. The curve showing the trajectory with respect to the earth, as drawn by Newton, was convex to the radius vector drawn to the initial position; and Prof. Rankine, in introducing the demonstration, gave an analysis showing that this drawing is correct. Many astronomical text-books, however, give the curve as a parabola concave to the initial radius vector, and the apparatus is designed to show the true state of the case.

The apparatus comprises a large horizontal rotatable table on which a sheet of paper is mounted. A weight carrying a tracing point is designed to slide easily over the paper and is attached to a thread which passes down through a hole at the centre of the turntable; a second weight is fastened to the other end of the thread, and hangs vertically below the turntable. The table is set in rotation by a gravity motor comprising a weight attached to a string, which is wound round the spindle, and when the motor has gone out of action, so that the speed of rotation is constant, the thread is automatically cut, so that the tracer-weight may be drawn in towards the centre from its initially peripheral position. The curve traced is very similar to that sketched by Newton.

The demonstration acquired a personal interest from the fact that Mr. Mather, who is now 85 years of age, became interested in the subject at the age of 14 through an accident which befell him when playing with a joy-wheel improvised from farm machinery.

ysica Lib.

THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 38.—PART 3.

APRIL 15, 1926.

Price to Non-Fellows **6s** *net, post free* **6/3.**

Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:

FLEETWAY PRESS, LTD.,
3-9, DANE STREET, HIGH HOLBORN, W.C.1.

1926.

THE PHYSICAL SOCIETY OF LONDON

1926-27.

OFFICERS AND COUNCIL.

President

PROF. O. W. RICHARDSON, M.A., D.Sc., F.R.S.

Vice-Presidents

(Who have Filled the Office of President.)

PRINCIPAL SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, C.B.E., M.A., LL.D., F.R.S.
SIR A. SCHUSTER, Ph.D., ScD., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. V. BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E, M.A., F.R.S.
ALEXANDER RUSSELL, M.A., D.Sc., F.R.S.
F. E. SMITH, C.B.E., F.R.S.

Vice-Presidents

PROF. F. LLOYD HOPWOOD, D.Sc.
D. OWEN, B.A., D.Sc.
E. H. RAYNER, M.A., Sc.D.
J. H. VINCENT, D.Sc., M.A.

Secretaries

PROF. A. O. RANKINE, O.B.E., D.Sc.
Imperial College of Science and Technology, S. Kensington, S.W.7.

J. GUILD, A.R.C.S., D.I.C., F.Inst.P.
Lalbagh, Park Road, Teddington, Middlesex.

Foreign Secretary

SIR A. SCHUSTER, K.B.E., Ph.D., Sc.D., F.R.S.

Treasurer

R. S. WHIPPLE
45, *Grosvenor Place,* S.W.1.

Librarian

J. H. BRINKWORTH, M.Sc., A.R.C.S.
Imperial College of Science and Technology, S. Kensington, S.W.7.

Other Members of Council

D. W. DYE, B.Sc.
A. FERGUSON, M.A., D.Sc.
E. A. OWEN, M.A., D.Sc.
SIR RICHARD PAGET, BART.
R. W. PAUL.
J. ROBINSON, M.Sc., Ph.D.
J. S. G. THOMAS, D.Sc.
W. S. TUCKER, D.Sc.
PROF. A. M. TYNDALL, D.Sc.
A. B. WOOD, D.Sc.

Assistant Secretary (Publications)

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley,* N.3.

XX.—CRITICAL DISCUSSION OF THE DETERMINATIONS OF THE MECHANICAL EQUIVALENT OF HEAT.

By Professor T. H. Laby, *M.A.*, *Sc.D.*, *F.Inst.P.*, University of Melbourne.

Received December 11, 1925.

ABSTRACT.

The principal recorded determinations of the mechanical equivalent of heat are critically discussed, and an attempt is made to correct them for errors not fully taken into account at the time when they were made. The results are weighted according to the relative importance attached to them by the author, and the weighted mean is given as 4·184 joules per calorie at 20 degrees.

THE value of the mechanical equivalent of heat has been critically discussed by Ames,* Luther and Scheel,† and E. H. Griffiths.‡ Since the publication of their articles further determinations of the mechanical equivalent have been made, and the ohm (106·3 cm. of mercury) is now known not to be exactly 10^9 electromagnetic units, as has been assumed in the past. Mr. E. O. Hercus and the writer have been engaged for a number of years upon a direct determination of *J*,§ which has required the earlier work to be carefully studied.

It is important to distinguish between the direct determinations of *J* and the indirect determinations by electrical methods, which yield what might be called the electrical equivalent of heat. Results by the two methods are only comparable in so far as the absolute values of the electrical standards (i.e., the E.M.F.s of the Clark and Weston cells, the mercury ohm, etc.) are known in terms of the corresponding electromagnetic units. So much attention has been given to the electrical units that they are now accurately known (to better than 1 in 10,000), and probably the accuracy with which they are known is more than ten times the accuracy with which *J* is known by direct experiment.

In arriving at the most probable value of *J* it is unavoidable that a weight should be given to each result, and there can be no doubt that certain determinations are more accurate than others, and the least accurate should not be given the same weight as the most accurate. Unequal weights are given below, but it is admitted that those given are arbitrary. In order that some judgment may be formed as to the accuracy of the various experiments they are briefly discussed.

Direct Determinations.—There are only two investigations of accuracy. Of Rowland's (1880) investigation, Ames says the "method of taking thermometric readings is liable to serious error." In the light of experiments made by Mr. Hercus and the writer, the pulleys used by Rowland would be subject to friction.

Reynolds and Moorby (1897) used, as is well known, a 70 H.P. Froude brake and continuous flow calorimeter with a temperature rise of 1·3°C. to 100°C. Steadiness of conditions is essential to such calorimetry. The speed varied, however, by as much as 3·3 per cent. in 30 minutes, and the rise of temperature by 2·7 C. in 120 seconds. An uncertain quantity of heat went to form steam bubbles in the water. The heat conducted along the steel shaft (two parts 3 in. long by 4 in. diameter) was not known with any certainty. The mean calorie in terms of which Reynolds and Moorby's result is obtained is not accurately known in terms of, say, the 20°C. cal.

---

* Rapports Congrès intern. d. Phys. (1900). Tome 1.

† V. Deut. phs. Ges., 10, p. 584 (1908).

‡ Dict. App. Phys., Vol. 1, p. 477.

§ For brevity *J* will be used for "mechanical equivalent of heat." Strictly, of course, *J* is the symbol for the ratio of two quantities of energy.

Electrical Equivalent of Heat.—Griffiths' (1894) experiments are notable for the exact limitation of the boundary of the calorimeter, the determination of the heat loss, and the elimination of the heat capacity of the calorimeter. The rate of energy input (2 to 6 watt), however, is the smallest used by any observer. Schuster and Gannon (1896) determined their temperature rise of about 2·25°C. by mercury thermometers. The six experiments upon which their value of J is mainly based gave values from 4·1884 to $4{\cdot}1940\times10^7$. They used a filter paper coulombmeter to determine the quantity of electricity used. Callendar and Barnes (1902) used platinum thermometers, and continuous flow calorimetry, realising very steady conditions and a small heat loss. Individual experiments in a series often agreed to 1 in 10,000. W. R. and W. E. Bousfield used both the continuous flow and rise of temperature calorimetric methods with mercury in glass thermometers. An uncertain amount of heat was lost by evaporation of water from the calorimeter, and the observers had difficulties with their resistances. Jaeger and Steinwehr (1921) have made a very carefully planned investigation at the Reichsantalt. Fifty kilogrammes of water were electrically heated by a power input of 800 watts. The electrical and platinum thermometry measurements were made with every refinement for accuracy. The rise of temperatures adopted were rather small, making extremely accurate thermometry necessary.

All the electrical determinations of J, if the results are to be expressed in ergs per calorie, require to be corrected for the electrical standards used, and some of the determinations require correction for the scale of temperature. These corrections can be best explained and made explicit by writing down the correction to be made to each determination which requires correction.

It is most important, if it is possible to do so, to correct the very accurate experiments of Callendar and Barnes. Barnes in 1909* discussed the corrections to be made to their results. There are three ways of arriving at the E.M.F. of the Clark cells (denoted by e_{CB} below) used by those observers. Barnes gives reasons for believing that the E.M.F. of cells in which the mercurous sulphate has been washed with water (as it was in the older cells) is 0·28 millivolts higher than cells prepared according to recent specifications. The E.M.F. of the latter is, according to Smith,† $e_{15}=1{\cdot}4333\,.\,10^8$ E.M.U. We have, then, $e_{\text{CB}}=(1{\cdot}4333+0{\cdot}00028)\,.\,10^8$ $=1{\cdot}43358\,.\,10^8$ E.M.U.

Further, Barnes states that

$$e_{\text{CB}}=1{\cdot}40666\,.\,\text{(Weston cell at 20°C. in 1900)}$$
$$=1{\cdot}40666\,.\,(1{\cdot}0188+0{\cdot}0003)\,.\,10^8=1{\cdot}4335\,.\,10^8\ \text{E.M.U.},$$

using the value given by Smith for the Weston cell, and correcting for the water washed mercurous sulphate. Callendar, however, in an appendix to Barnes' Paper, implies that King's experiments with the Clark cell give

---

* Proc. Roy. Soc., 82, p. 390 (1909).

† Dict. App. Phys., Vol. 2, p. 271.

$$e_{\mathrm{CB}}=1{\cdot}4334\ .\ \text{semi-absolute volts}=1{\cdot}4341\ .\ 10^8\ \text{E.M.U.}$$

I have assumed $e_{\mathrm{CB}}=1{\cdot}4338\ .\ 10^8$ midway between the above values. Barnes,[*] assuming $e_{\mathrm{CB}}=1{\cdot}43325\ .\ 10^8$ E.M.U., and 1·01358 B.A. unit$=1$ true ohm (i.e., 10^9 E.M.U.) found $J=4{\cdot}1783\ .\ 10^7$ erg per 20° cal. The energy input was given by an expression of the form $Ee\ t/R$, and so the corrected value is for *Barnes*

$4{\cdot}1783\ .\ 10^7\ .\ (1{\cdot}4338/1{\cdot}43325)^2\ .\ (1/1{\cdot}0005)=4{\cdot}1795\ .\ 10^7$ erg per 20° C. cal. where the factor 1/1·0005 corrects the resistance. No correction to the hydrogen scale is needed according to Professor Callendar (see below). In all the electrical determinations of J, except that of Schuster and Gannon, standards of resistance have been used based on the 106·3 cm. of mercury ohm, but it is now known that that ohm—it is the international ohm—is $1{\cdot}0005_2\ .\ 10^9$ E.M.U.[†]

Griffiths and Schuster and Gannon used Clark cells standardised against the Cavendish laboratory cells by Glazebrook and Skinner. For these cells I assume $e_{15}=1{\cdot}4336\ .\ 10^8$ E.M.U. We get the following corrected values of J:—

Griffiths[‡] : $4{\cdot}199\ .\ (1{\cdot}4336/1{\cdot}4342)^2\ .\ (1{\cdot}0004/1{\cdot}0005)\ .\ (1{\cdot}0011)^{-1}\ .\ 10^7$

$=4{\cdot}1904\ .\ 10^7$ erg per 20°C. cal.

The factor 1·0004 corrects from the air to the hydrogen scale, and $(1{\cdot}0011)^{-1}$ from the 15° to the 20° cal.

Schuster and Gannon[§] : $4{\cdot}1917\ .\ 10^7\ (1{\cdot}4336/1{\cdot}4340)\ (1{\cdot}00017)^{-1}=4{\cdot}1898\ .\ 10^7$ erg per 20° cal. These observers used a filter paper silver voltameter, which may deposit from 1 to 10 in 10,000 more silver per absolute coulomb than they assumed.

W. R. and W. E. Bousfield[||] : $4{\cdot}1755\ .\ 10^7\ (1{\cdot}0188/1{\cdot}0184)^2\ .\ (1{\cdot}0005)^{-1}=4{\cdot}1767\ .10^7$ erg per 20° cal.

Jaeger and Steinwehr[¶] : $4{\cdot}1800\ .\ 10^7\ (1{\cdot}0188/1{\cdot}0183)^2\ .\ (1{\cdot}0005)^{-1}=4{\cdot}1821\ .\ 10^7$. The E.M.F. of the Weston cell at 20°C.$=1{\cdot}0183$ international volt$=1{\cdot}0188\ .\ 10^8$ E.M.U. The Bousfields assumed 1·0184 int. volt.

The value given for *Rowland* in the following table is based on Day's correction of his results to the hydrogen temperature scale ($4{\cdot}181\ .\ 10^7$ at 20°C. and 4·188. at 15°C.), and corrected for his temperature range, assuming 15° cal./20° cal.$=1{\cdot}0011$. Reynolds and Moorby's results, $J=4{\cdot}1832\ .\ 10^7$ erg per mean cal., is in terms of the calorie 1·3° to 100°C. Dr. Ezer Griffiths and Mr. Awbery kindly inform me that 1 mean cal. $=1{\cdot}002_2$ cal. at 20°C., according to data which they have prepared for the International Critical Tables. According to Professor Callendar, the ratio is 1·0016. I use 1·002.

---

[*] **Phil. Trans., p. 261 and p. 172, A 199 (1902).**

[†] **Smith, loc. cit., p. 247.**

[‡] **Griffiths, Phil. Trans., p. 314, A 186 (1895); in this author's 1894 Paper different values are given.**

[§] **Phil. Trans., p. 458, 186 (1896).**

[||] **Phil. Trans., p. 236, A 211 (1911).**

[¶] **A. d. P., p. 365, 64 (1921).**

*Reynolds and Moorby** : $J = 4{\cdot}1832 \,.\, 10^7 \,.\, (1{\cdot}0002/1{\cdot}002) = 4{\cdot}1758 \,.\, 10^7$ erg per 20° cal.
The value of the mean calorie is, however, somewhat uncertain, as the determinations of the specific heat of water from about 50° to 100° are discordant for data of this kind.

Mechanical Equivalent of Heat.
(Hydrogen temperature scale.)

	Erg per 20°C. cal.	Wgt.
Direct determinations—		
Rowland	$4{\cdot}1822 \,.\, 10^7$	2
Reynolds and Moorby	$4{\cdot}1758 \,.\, 10^7$	1
Indirect electrical determinations—		
Griffiths	$4{\cdot}1904 \,.\, 10^7$	1
Schuster and Gannon	$4{\cdot}1898 \,.\, 10^7$	1
Callendar and Barnes	$4{\cdot}1795 \,.\, 10^7$	2
Bousfields	$4{\cdot}1767 \,.\, 10^7$	1
Jaeger and Steinwehr	$4{\cdot}1821 \,.\, 10^7$	2
Weighted mean	**4·182** $. \, 10^7$	

Miculescu and Rispail have also made determinations. The corrected results are entered in the table above, and a weighted mean value derived. The agreement between the different values entered is not very close.

The Mean Calorie.—The value of *J* entered against Reynolds and Moorby is evidently low. Is the error in their experiments, or is it in the value of the ratio mean cal./20°C. cal. used to convert their result to the 20° cal.? The question is an important one, as the mean calorie is the most convenient heat unit for expressing the thermal properties of steam, and it is desirable that its value in terms of the erg should be known. Possibly the most accurate way of finding the ratio mean cal./erg is from the ratios mean cal./latent heat of steam and erg/latent heat of steam. Carlton Sutton,† using the Joly steam calorimeter, found the latent heat of steam equal to 538·88 mean cal.

DISCUSSION.

Mr. F. E. Smith said that he had little faith in the values of physical constants obtained by applying corrections long after the date of the observations. The Clark cell used in one instance had come into his hands, and was found to have an E.M.F. less than 0·1 volt; no one could say what its original E.M.F. was. He would be inclined to attach more weight to electrical than to mechanical determinations of *J*.

Mr. T. C. Sutton: Among points of interest too numerous to mention in the time at our disposal, Prof. Laby refers to the use of the latent heat of steam as a means of determining the mechanical equivalent of the mean calorie. My own experience (Proc. Roy. Soc., A93, p.155, 1917) with various forms of steam calorimeter has convinced me that it can be developed into an instrument of great accuracy. In investigations such as we are now considering it presents many advantages, not the least of which is the fact that all thermometers can be dispensed with. The value obtained in this way for the latent heat of steam is *538·9* mean calories. In his work on the total heat of steam, Callendar derived (from electrical measurements) the value *540·2* twenty-degree calories. Consequently, if the two values were to agree, the ratio of the mean calorie to the twenty degree calorie had to be *1·002,4*. The accepted value at the time was *1·001*, which represented a discrepancy too great to be attributed to any obvious experimental error. I had not the courage, at the time, to blame the accepted value of the mean calorie. It is therefore with surprise, and much satisfaction, that I now learn that Dr Griffiths and Mr. Awbery obtain the value *1·002,2*, and are using this as the official figure of the International Tables. This gratifying reconciliation, after a lapse of ten years, emphasises the reliability of steam calorimetry, and places the value of the latent heat of steam at the experimentally determined figure *538·9* mean calories. At the outbreak of war in 1914 I had in mind also a determination of the latent heat of steam in (*a*) electrical units and (*b*) mechanical units (methods indicated by lantern slides), and regret that at the moment I see no prospect of myself carrying these investigations to their logical conclusion.

---

* Phil. Trans., 190 (1897).

† Proc. Roy. Soc., p. 155, A 93 (1917).

Mr. J. H. **Awbery** : The ratio between the mean calorie and the 20° calorie which I quoted to Professor Laby was deduced from a consideration of all the published determinations. It was higher than the number commonly accepted previously, chiefly because of the figures of Jaeger and Steinwehr (Sitz. d. Berl. Akad., p. 424, 1915). I should like to emphasise that the agreement of the different investigations is such that no reliance should be placed on the fifth significant (fourth decimal) figure in this ratio.

Dr. **Ezer Griffiths** : Prof. Laby's Paper revives interest in a subject which occupied the attention of many physicists a quarter of a century or so ago. One cannot but admire the courage of an investigator who sets out to determine a thermal constant to an accuracy of one part in five thousand, for it will probably be as difficult to do so as to determine an electrical unit to one part in fifty thousand. Before commenting on Prof. Laby's apparatus, I would like to make a few remarks on the Paper. I view with certain misgivings attempts to correct old work unless made by the investigators themselves, as they alone are acquainted with all the facts concerning their apparatus. In the present instance many of the investigators whose work had been corrected by Prof. Laby are still living, so they can make their views known before Prof. Laby writes his final account. In the publication of work of high precision some authorities advocate the insertion of the data in great detail, so as to facilitate subsequent correction. The plan I would like to suggest is that the investigator should take steps to preserve his apparatus, so that the experiments can be repeated with such modifications as experience dictates. It will, I think, be generally admitted that the development of the method and the technique absorbs most of the time in an investigation, so a repetition would not be a formidable undertaking. When our President designed the Lorenz apparatus for the determination of the ohm, he so arranged matters that all the essential measurements could be checked at any time. If anyone in future were dissatisfied with the value ascribed to the ohm, he could re-determine it, basing his measurements solely on his own metre rule and clock and using this apparatus. As regards methods for the determination of *J*, the simplest to operate at the present time is the electrical. The electrical units are now known to an accuracy of at least one part in 10,000 ; it is improbable that a calorimetric determination can be made to one part in 5,000, one of the reasons being that we do not know of a heat insulator comparable with a first class electrical insulator, such as amber. I would further advocate working on a large scale, so that corrections for heat capacity of the container, stirrer, etc., would be relatively very small. I consider that the weight attached by physicists to Reynolds and Moorby's result is an unconscious tribute to large scale experiments, and I am surprised that no one has repeated the test using standard thermometers to measure the temperature rise over a narrow range, instead of between 0° and 100°C. The objections raised by Prof. Laby to Reynolds and Moorby's experiments could be overcome with modern engineering appliances.

Mr. G. M. **Clark** : In re-introducing myself to the meetings of the Society after an absence of more than 25 years spent abroad, I may say that it was my pleasure and honour to be associated with Griffiths from 1887 to 1892 during the period of making the determination of *J*, and I warmly welcome the proposal of the author to revise the value of this constant. I doubt whether much is gained by discussing the results of other observers by making known corrections that arise through the light of later knowledge. Every physical determination is a shot at a target, and by the removal of certain errors it is by no means certain that the remainder give a better probable value for the centre of the target. The tables put forward by the author are, however, not only of use for the point that the author wished to make—namely, the necessity for revision—but they are also of use as showing that the halo of nebulosity surrounding any physical determination is probably greater than the original experimenter cared to acknowledge to himself. I am also of opinion that the only person who can revise any old determination is the person who made it. One of the obscure causes of uncertainty about which very little is said is the formation of steam bubbles or any evaporation that takes place from the calorimeter either in steady flow or other form. When it is remembered that it takes about 500 calories to evaporate water and only 1 calorie to heat it up a degree, it is evident that very little evaporation, which might take place in the body of the water to be heated, would produce an error in the direction of reducing the final value. It is, therefore, almost essential to use a different method as Griffiths has done, heating first by stirring alone and then with increasing current, and calculating from the differences the work done. It is rather a matter of luck whether this eliminates the obscure uncertainties that are bound to occur in all calorimetry. I admire very much the author's apparatus and equipment and contrast it with our own of nearly forty years ago, when storage batteries were unknown and part of our time for experimental work was taken up with fitting up Bunsen's cells with strong nitric and sulphuric acids. It was impossible at that time to get small electric motors for driving stirrers, etc., and even the laboratory was not lighted with electric light. Over two years of our time were spent in research into thermometry, which was a side show to the main determination, but involved such work as the development of the platinum resistance thermometer, and the fixing of its standardisation point, the boiling point of sulphur. I envied the author his being able to start up with so much modern equipment, and though the difficulty of measurement increases by about the fifth power of the accuracy, I hope that this modern equipment will remove about three of them and not more than the square would be left for the author to contend with. I wish him every success in his work, and feel that he can do it whole-heartedly as one who has already been thoroughly over the ground in every detail.

Prof. E. H. **Griffiths** (communicated): I regard a critical discussion, such as given by Prof. Laby, as of high value. Had I time I should have wished to comment on his methods of reduction and the conclusions he arrives at. I will, however, only refer to his remarks upon my own determinations. In line 18 on page 171 he states, " Griffiths : 4·199." In Dict. App. Physics, Vol. I., p. 493, Table X., I give what I consider as the final value resulting from my own experiments—viz., 4·184 cals. at 20°C. of the hydrogen scale. Curiously enough, this is identical with the " weighted mean " arrived at by Prof. Laby. In this 1924 article I have given my reasons for each step in the reductions. I confess that it appears to me that it is the final, and not the earlier, conclusions of an author which should be quoted.

Prof. H. L. **Callendar** (communicated): The " Continuous Electric Method " of calorimetry was designed with the primary object of determining the variation of the specific heats of water and mercury over the range 0°C. to 100°C., for which it appeared to be the most suitable method available. Careful attention was paid to the details of platinum thermometry and temperature regulation, and the *constancy* of the standard cells and resistances employed was verified with the utmost precision. The results for the variation of the specific heat of water were subsequently confirmed by an independent method, called the " Continuous Mixture Method " (Phil. Trans., A, 212, p. 1, 1912). The several formulæ previously employed were combined into a single equivalent formula possessing special advantages, which gives the following values for the ratios of the mean calorie and the 15° cal. to the 20° calorie ; mean calorie 1·0016, 15° calorie 1·0012, respectively. Reynolds' value for the mean calorie corrected for the range 0°C. to 100°C. becomes 4·1837 joules per cal. in place of 4·1832 for the range 1·3°C. to 100°C., and corresponds to a value 4·1770 for the 20° calorie. The value 4·1932 given by Prof. Laby is probably an accidental error.

The most unsatisfactory point in the reduction of Rowland's observations to the hydrogen scale is that the thermometers could not be compared with the gas thermometer under the actual conditions of the experiment on a rapidly rising temperature. This is one of the reasons why it is necessary to employ platinum thermometers directly in experiments of this nature. The zero lag of a mercury thermometer on a changing temperature tends to give results which are too small for the temperature interval, or too large for the value of J. The correction from the nitrogen to the hydrogen scale was taken as +3 parts in 10,000 from Chappuis' corrected results (Phil. Trans., A, 199, p. 101, 1902). It was found that this correction was compensated throughout the range 0°C to 100°C. by a small correction of opposite sign due to variation of the temperature gradient in the flow-tube. Both corrections were omitted by Barnes in his final table, which, therefore, remains correct (loc. cit., p. 129) as if they had both been included.

In the reduction of the results to absolute units (joules per gm. cal.) at any temperature, the conventional value 1·4342 int. volts was assumed for the Clark cells, and the international ohm was taken as being equal to the absolute ohm. The result obtained in this way is given as 4·1838 joules per gm. cal. at 20°C. in Barnes' table 1902. The experiments of Ayrton and Mather with the Lorenz apparatus, destined for McGill College, and those of King with the electrodynamometer in 1897, had already shown that this result was too high, but the absolute values of the electrical units required further investigation. Barnes' ratio 1·40666 of the Clark cell to the Weston cell has since been confirmed, and the cells set up with washed mercurous sulphate in 1900 exceed the modern cells by 0·30 millivolt. Adopting these data, we agree with Prof. Laby in finding 1·4335 abs. volts for the old Clark cell in place of the assumed value 1·4342. If we also take the international ohm as being 1·0005 absolute ohm, Barnes' original results require to be reduced by nearly 10 in 10,000 for the cells, and by 5 in 10,000 for the ohm, giving Callendar and Barnes 4·178 joules per gm. cal. at 20°C. I have generally taken the value 4·180, giving greater weight to Rowlands' direct determination.

Mr. W. R. BOUSFIELD (communicated): With reference to the determination by W. R. and W. E. Bousfield, it is said that the "observers had difficulties with their resistance." This idea must have arisen from the fact that we investigated the difficulties with a wire resistance for heating, and abandoned it, and used instead the new device of a "mercury thermometer resistance." This was shown to be extraordinarily accurate, and was used throughout with excellent results. It is also stated that "an uncertain amount of heat was lost by evaporation of water." This was only the case with high temperatures. From 0° to 40° this heat loss was determined with great accuracy.

The comparative figures for our determinations and those of Callendar and Barnes do not appear to be correctly stated in Prof. Laby's Paper. Our results (*see* p. 241 of our Paper) from 13° to 55° mean value were—

$$J = 4·182.$$

Callendar and Barnes for the same interval were—

$$J = 4·175.$$

Yet Prof. Laby seems almost exactly to *reverse* these figures. I do not know what sort of corrections can have been applied to produce these figures. Our results were subsequently confirmed by an independent investigation.* The question of wire resistances was taken up in a subsequent Paper in the Proc. Roy. Soc. by Glazebrook, Bousfield and F. E. Smith, the reference to which I have not at hand.

AUTHOR'S reply: I think that some of the electrical standards used in the *J* experiments of the past can be expressed in electro-magnetic units. No doubt the values of the older standards of E.M.F. are quite uncertain, but the E.M.F. of the Weston cells used by the Bousfields and by Jaeger and Steinwehr is known, and so is the value of the standards of resistance used even in 1892. The ohm appears to have been pretty accurately 106·3 cm. of mercury, or $1·0005 \times 10^9$ E.M.U. for over twenty years. I agree with practically all that Prof. Callendar says, and I have accordingly made certain changes in the Paper above. In correcting our own experiments to 20°C., Mr. Hercus and I have used for some years Prof. Callendar's 1912 formula for the variation of the specific heat of water with temperature, as being the most accurate available. In view of his statement that Barnes' results are in effect already corrected to the hydrogen scale I now omit that correction. That his results are effectively on that scale is not, I think, mentioned in Barnes' Paper, and I overlooked that it is mentioned in Prof. Callendar's.

Dr. E. H. Griffiths' results are very valuable for the reasons stated in the text, but the E.M.F. of the Clark cell which he used is uncertain.

With reference to several criticisms, it is necessary to stress that on the pages quoted in the footnotes to my Paper will be found the authority for the data which have been used in it.

---

* See Bousfield, Specific Heat of Water, Proc. Roy. Soc., A, 93, p. 588 (1917).

XXI.—THE PRESENT STATUS OF THEORY AND EXPERIMENT RELATING TO SPECIFIC HEATS AND THE CHEMICAL CONSTANT.

By F. Ian G. Rawlins, Trinity College, Cambridge.

Received October 5, 1925.

(*Communicated by* Dr. D. Owen.)

Abstract.

The theoretical and experimental aspects of the specific heats of solids, liquids and gases in the light of present knowledge are discussed. Possible lines of advance have been indicated for solids in view of the progress now being made in X-ray crystallography, and the importance of further experimental work on compressibilities and elastic constants is suggested. Tentative views on the specific heat of liquids are given. In gases the quantum theory of rotational heat is shown to fail to account satisfactorily for the behaviour of hydrogen at low temperatures. The chemical constant of monatomic and diatomic substances is discussed, both from a thermodynamic and from a statistical point of view. Current views on the nature of this constant are described. The theory of gaseous degeneracy and its bearing upon specific heats and chemical constants is reviewed.

In this paper an attempt will be made to convey some idea of our present knowledge, both theoretical and experimental, of the specific heats of solids, liquids and gases. This theme can perhaps most profitably be treated by including a discussion of the chemical constant, both in its statistical aspect and also in regard to its function as a constant of integration in the vapour-pressure equation. Recent work has brought to light some interesting discrepancies between the value of the chemical constant thus found and that deduced from dissociation equilibria. Attention will also be directed to the subject of Gaseous Degeneration, to which Eucken, Mache and Bennewitz have given much attention of late years, and which affords an opportunity of studying the theory of specific heats and chemical constants in close relationship.

For clarity of treatment the following scheme suggests itself:

(1) *Specific Heats.*
    (*a*) Solids.
    (*b*) Liquids.
    (*c*) Gases.

(2) *Chemical Constants.*
    (*a*) Monatomic substances.
    (*b*) Diatomic substances.

(3) *Gaseous Degeneration.*
    Both with particular reference to specific heats, also to chemical constants.

(4) *Summary.*

With regard to the particular weight attached to theory and experiment, the aim is to describe experimental results where they confirm or fail to bear out the theory. Except in one instance (in the section on the specific heats of liquids), actual laboratory arrangements are not described. The special calorimetric apparatus devised by Nernst for work on the specific heat of solids is hardly novel enough to need detailed attention here.

(1) SPECIFIC HEATS.

(*a*) *Solids.*

Excluding the early work of Einstein and the semi-empirical attempts of Nernst and his pupils, the first theory of the specific heats of solids embodying a quantum partition of energy was due to Debye. His conception, however, includes the classical view of elasticity, leaving out of consideration the atomic nature of the substance. In fact, it treats solid bodies as structureless continua. In reality, assuming that the body consists of N atoms, there cannot be more than $3N$ natural frequencies. Debye obtains the upper limit of the elastic spectrum $\nu_{\text{max.}}$ by stopping arbitrarily at the $3N$th natural period. It is interesting to inquire how the value of $\nu_{\text{max.}}$ formed from the elastic constants compares with the value of $\nu_{\text{max.}}$ as deduced from specific heat measurements, using Debye's formula.

A table given by Eucken on page 102 of his "Grundriss der physikalischen Chemie" shows that $\nu_{\text{max.}}$ (elasticity) is generally some 5 per cent. higher than $\nu_{\text{max.}}$ (thermal). It is only by stressing the weakest part of Debye's theory—i.e., that the vibrations in a solid fall off suddenly at a perfectly defined frequency, $\nu_{\text{max.}}$—that agreement could be expected. The agreement between $\nu_{\text{max.}}$ (thermal) and the frequency deduced by Lindemann's formula is erratic, as might be foreseen from the consideration that it is only at the melting point temperature itself that it has any very definite physical basis.

The difference, however, is as little as 3 per cent. between $\nu_{\text{max.}}$ (thermal) and ν (Lindemann) for monatomic elements of low melting point, whereas for the diamond it amounts to some 15 per cent.

Generally speaking, Debye's theory is fairly well confirmed by experiment for monatomic substances, as well as the corollary that at very low temperatures the molecular heats of all solids (not necessarily monatomic) should be proportional to the third power of the absolute temperature. Debye's equation demands that the molecular heats of solids should vanish at the absolute zero, approaching the classical value $3R$ when T/θ is greater than 0·9 (T is the absolute, θ the "characteristic, temperature," which for the majority of substances lies between 100 and 200). Several attempts have been made to extend Debye's theory to solids other than chemical elements. The conception of a solid as a mass of similar atoms now gives place to that of a collection of similar molecules. Within each molecule exist vibrations of a type which will be considered later in connection with the specific heat of gases. For a solid consisting of N molecules, if we sum the contributions from the vibrations within the molecules and the motions of the molecules themselves, an expression of the form

$$E=9N\int_0^{\nu_{\text{max.}}}\frac{h\nu^3}{e^{\frac{h\nu}{KT}}-1}\cdot\frac{d\nu}{\nu^3_{\text{max.}}}+N\Sigma\frac{h\nu_1}{e^{\frac{h\nu_1}{KT}}-1}\quad\ldots\ldots\ldots\ldots\quad(1)$$

results for the energy. The summation is to be extended over all the internal molecular vibrations. For a diatomic substance the summation reduces to a single "Einstein" term. In confirmation of this formula, Nernst* shows if by ν_1 is understood the frequency of a Rubens absorption band in the infra-red, very fair agreement is obtained with the experimentally-determined values of the specific heats of simple compounds. The conception involved in (1) is, however, very crude. Clearly, interaction of a very complicated kind takes place between the whole assembly of atoms within the solid, so that it is not justifiable except as the roughest of approximations to regard the vibrations as being capable of being split up into those within the molecule and those in which the molecule as a whole is concerned. It is easy to see that if all the atoms in a solid are taken to be alike, (1) does not reduce to the simple Debye expression for the energy of an element. Schaefer has recently shown* that Debye's T^3 law cannot be valid at extremely low temperatures; in such a region an exponential law is demanded.

---

* Vorträge über die kinetische Theorie der Materie, p. 81 (1914).

Better results are likely to be obtained by the use of the Born and Karman theory,† which takes account of the crystal lattice. Since from the work of W. H. and W. L. Bragg and others the type of lattice is known with certainty for a large number of crystals (both elements and compounds), it may be expected that considerable progress will occur along these lines. A particularly interesting point is the question of the molecular lattice, which is of some consequence in one of the writer's papers. From evidence which is given there it appears that the crystal structure of the halogen hydrides is very different from that of binary salts, such as NaCl. The suggestion is that the unit is not the atom (or ion), but the molecule. A recent paper‡ has given some grounds for thinking that the same is true for the halogens.

For iodine, however, a single frequency $\beta\nu=106$ represents the specific heat admirably, from which it might be inferred that iodine is atomic in the solid state (as opposed to a molecular grouping). The two allotropic forms of zinc sulphide, zincblende and wurtzite might prove of interest in this way. The lattice of ordinary zincblende is certainly atomic (Eucken's "Grundriss," p. 480), but in wurtzite the structure is molecular (Eucken, loc. cit.). The specific heat of zincblende can be fitted excellently to a Debye function with $\beta\nu=175$. An experimental determination of the specific heat of wurtzite, especially at low temperature, might prove illuminating. One would expect that, in view of its molecular structure, it would deviate considerably from Debye's curve.

Measurements of specific heats usually refer to C_p (the specific heat at constant pressure), whereas for a comparison with theory C_v (the specific heat at constant volume) is required. For metals, the usual method of obtaining C_v is by means of the equation

$$C_p - C_v = \frac{wa^2eT}{\rho} \qquad \ldots\ldots\ldots\ldots \quad (2)$$

where w is the atomic weight, a the coefficient of cubical expansion, e the volume elasticity and ρ the density. When we come to crystalline salts the lack of data necessary for (2) makes it imperative to seek a different method. Nernst and Lindemann§ obtain a formula

$$C_p - C_v = C_p{}^2TA \qquad \ldots\ldots\ldots\ldots \quad (3)$$

where A is a constant characteristic of the substance which may be deduced from measurements of the compressibility and coefficient of expansion made at one temperature. Really, equation (3) rests upon Grüneisen's observation that the coefficient of expansion is proportional to the atomic heat. According to Eucken ("Grundriss," p. 485), the compressibility k of a crystal is related to the grating constant d by the simple equation

---

* Zeit. für Physik, 7, p. 287, (1921).

† Born, Der Dynamik der Kristallgitter, 2nd edition.

‡ Friederich, Zeit. für Phys., 31, p. 813 (1925).

§ La Théorie du rayonnement et les quanta, p. 265 (1912).

$$K=5{\cdot}68\times10^{18}\,.\,d^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The agreement with observation is very good, as the following examples show. They are typical of a fair number of results.

	$K_{\text{obs.}}$	$K_{\text{from (4)}}$
NaCl	$4{\cdot}1\times10^{12}$	$3{\cdot}56\times10^{12}$
KI	$8{\cdot}6\times10^{12}$	$8{\cdot}68\times10^{12}$
TlCl	$4{\cdot}7\times10^{12}$	$4{\cdot}69\times10^{12}$

The importance of this is for the evaluation of the constant A in equation (3) if, as is often the case, the crystal structure is known.

Naturally, it is hardly possible to use (4) for crystals possessing a molecular lattice.

In considering the molecular heats of solids as a function of the temperature, great care is needed to make sure that any allotropic changes are observed and their heats of transformation recorded. Thus, there are three forms of solid oxygen, two of solid nitrogen, two of carbon monoxide, two at least of iodine (the transition being extremely slow). In connection with the deduction of the chemical constant from thermodynamical equations, these transformations are of considerable importance.

It remains now to discuss the specific heat of solids at high temperatures.

The fact is that in the neighbourhood of 1,000°C. the atomic heat at constant volume of certain solids has been found to exceed the classical value $3R$ very considerably. There must therefore be some source of internal energy to be taken into account in addition to the atomic vibrations. Presumably, this is due to the movements of electrons within the atom. This electronic energy is negligible at low temperatures compared with that possessed by the atoms, but by no means so at high temperatures where it will make itself felt in the atomic heat.

Koenigsberger* has attacked this problem, and considers that C_v should reach the value 9 (instead of 5·95) if the vibrations of the electrons are taken into account. The following are examples :—

Metal.	Temp.-Range.	C_v
Ag	900°C.	6·7
Cu	900°C.	7·1
Al	650°C.	7·7
Ni	1,150°C.	7·9
Sn	1,100°C.	9·2
Fe	1,200°C.	9·6

(*b*) *Liquids.*

A satisfactory discussion of the specific heats of liquids is difficult, in that there is at present no guiding principle possessing physical significance. In this section reference will be made to the suggestions of Honda,† as being the only attempt—

---

* Zeit. für Electrochem., 17, p. 289 (1911)

† Phil. Mag., 45, p. 189 (1923).

as far as the writer is aware—to give a tentative theory of the subject. Before going into this, it may be convenient to state a few general results which have been accumulated in recent years.

In general, the specific heat of a liquid is of the same order of magnitude as that of the same substance in the solid state, though inclined to be higher. C_p usually rises considerably with the temperature, either linearly or as a curve which gets steeper with increasing temperature.

There are some interesting exceptions showing great irregularity, which indicates a change of molecular constitution. In liquid sulphur, for instance, there is a sharp maximum at 160°, which is clearly connected with the existence of the two molecular species S_λ and S_μ (probably S_8 and S_6).

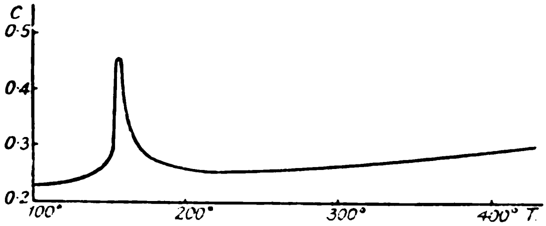


FIG. 1.—HEAT CAPACITY PER GRAM OF LIQUID SULPHUR (LEWIS).

The heat absorbed is largely devoted to increasing the amount of the latter at the expense of the former. Williams and Daniells* have recently examined a number of organic liquids in their adiabatic calorimeter. Benzene, for example, shows a number of irregularities indicative of molecular changes. The authors find that water acts as a catalyst in bringing about the transformation from one molecular species to another. They suggest that differential specific heat determinations would offer a good way of studying the phenomenon of association in liquids.

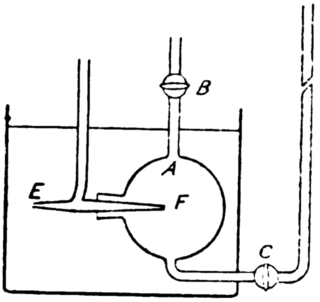


FIG. 2.—ARRANGEMENT FOR THE DETERMINATION OF THE HEAT CAPACITY OF LIQUIDS.

A method suggested many years ago for measuring the specific heats of liquids has lately been revised in a modified form by Barus.† It depends upon the thermodynamical equation

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p.$$

---

* Amer. Chem. Soc. Journ., 46, p. 1569 (1924).

† Publ. Carnegie Inst., 249, 9, 4 (1919).

The flask A contains the liquid under investigation. It is placed in a thermostat and brought to an even temperature, recorded by a sensitive thermocouple EF. The cock B (hitherto open to maintain atmospheric pressure) is now closed and C opened. The quotient of the increase in temperature by the applied pressure gives $\left(\frac{\partial T}{\partial p}\right)_s$. If the coefficient of expansion $\left(\frac{\partial v}{\partial T}\right)_p$ is known, C_p follows.

Honda's theory of the specific heat of liquids may be outlined thus. It applies mainly to monatomic substances. The atoms in a solid perform vibrations according to the usual theory with the mean energy $3Rf\left(\frac{\theta}{T}\right)$, θ being the characteristic temperature. In addition to this, Honda assumes that the atoms have some kind of rotational oscillations about their centre of gravity in the solid, a constraint being imposed by the directive forces of neighbouring atoms. Fusion is supposed to take place when the energy of the rotational oscillations becomes so great that the atoms execute continuous rotations. Honda neglects the work done against cohesion, and explains the latent heat of fusion as the energy which these new degrees of freedom of continuous rotations must acquire.

Lindemann discusses these assumptions, and shows that on the whole they are untenable.

For instance, it is not difficult to see that a characteristic temperature of the order 5×10^6 would be required, which is of a totally different order from the figures usually considered. Again, a negative heat of fusion would result, as Lindemann shows. However, Honda arrives finally at the result that the difference $C_v - C_v{}^1$ between the atomic heats of the liquid and solid phases of the same substance is equal to $R\left(\frac{n}{2} - 3e\right)$, when n is the number of degrees of freedom of the atoms in the liquid, and e lies between 0 and 0·5.

(c) *Gases.*

(i) *Monatomic.*—Here there are three degrees of freedom (translational). On the classical theory, the molecular heat C_v is constant and equal to $\frac{3}{2}R$. This is in accordance with experiment up to the highest temperatures. At very low temperatures Eucken has found marked deviations from the value $2{\cdot}98 \frac{\text{cals.}}{\text{degree}}$. The significance of this effect will be discussed in the Section dealing with gaseous degeneration.

(ii) *Diatomic.*—The number of degrees of freedom is now six. On the classical theory of equipartition, provided all the degrees are effective, the molecular heat of an ideal diatomic gas is independent of the temperature and equal to $\frac{7}{2}R$. This is contradicted by experiment. Eucken has found that at low temperatures hydrogen behaves as a monatomic gas with $C_v = \frac{3}{2}R$, corresponding to the translational degrees alone. Also at 2,000°C. the molecular heat is only 6·5 instead of 6·98; i.e. $\left(\frac{7}{2}R\right)$.

Generally speaking the atomic vibrations in a diatomic gas are of high frequency. ν is of the order 10^{14}, falling in the short infra-red. According to the quantum theory, the probability that the vibrations will contribute an appreciable amount to the molecular heat becomes very small, even if the temperature is not very low. The molecular rotations are of much lower frequency (of the order 10^{12}), and consequently persist at a temperature at which the vibrational term would be negligible, since the quantum $h\nu$ associated with rotation is much smaller than that associated with vibration. At any given temperature, therefore, the chance of possession of a rotational quantum is greater than that of a vibrational quantum. With decreasing temperature the probability of the possession of a quantum of any size grows less, so that at very low temperatures even $C_{\text{rot.}}$ vanishes, leaving the translational term alone.

It will be convenient to write the specific heat of a diatomic gas in the form

$$C_v = C_{\text{trans.}} + C_{\text{rot.}} + C_{\text{vib.}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

and to consider the contributions separately. Excluding for the present the possibility of "degeneracy," $C_{\text{trans.}}$ is constant and equal to $\frac{3}{2}R$.

$C_{\text{rot.}}$ has been investigated by various workers. On the basis of the dumb-bell model, Reiche* arrives at a general expression of the form

$$C_{\text{rot.}} = R\sigma^2 \frac{f(x)}{g(x)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where $\sigma = h^2/8\pi^2 JKT$ (J is the moment of inertia), and $f(x)$ and $g(x)$ are series in ascending powers of x, where $x = e^{-\sigma}$. For low temperatures $\frac{C_{\text{rot.}}}{R}$ tends to zero, and at higher temperatures to unity, as demanded by the classical theory.

In order to obtain a steadily rising curve it is necessary to make certain assumptions regarding the *a priori* probabilities or weights of the different quantum states. Thus, it appears that the rotationless state $n=0$ must be suppressed (otherwise the curve rises to an intermediate maximum before reaching $C_{\text{rot.}} = R$), and, further, the best agreement with experimental points, in the case of hydrogen, is obtained when the weight n or $2n$ (indistinguishable from one another) is assigned to the nth quantum state. None of the curves computed by Reiche, or the other workers along similar lines, succeed in accounting for all the observations, especially those in the neighbourhood of 200° absolute. It must be admitted that at present this problem remains unsolved.

With respect to the contribution $C_{\text{vib.}}$, assuming that the atomic vibrations can be taken as independent of the molecular rotations, this can be represented by a " Planck " term as for a simple oscillator

$$C_{\text{vib.}} = R\left(\frac{h\nu_0}{KT}\right)^2 \frac{e^{-\frac{h\nu_0}{KT}}}{\left(1 - e^{-\frac{h\nu_0}{KT}}\right)^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

This is analogous to the expression used in the theory of the specific heat of solids, except that there the number of degrees of freedom is three, whereas here it is one. The frequency ν_0 should correspond to the difference between the centres of successive bands in one family in the band-spectrum of the gas.

---

* Ann. der Phys., 58, p. 657 (1919).

This "Planck" term becomes of some importance in the deduction of the chemical constant, as Cox* has shown in his work on iodine and bromine.

The expression for C_v thus becomes

$$C_v=\frac{3}{2}R+\sigma^2R\frac{f(x)}{g(x)}+R\left(\frac{h\nu_0}{KT}\right)^2\frac{e^{-\frac{h\nu_0}{KT}}}{\left(1-e^{-\frac{h\nu_0}{KT}}\right)^2} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

For large values of T, the second and third terms tend to R (giving C_v the classical value $\frac{7}{2}R$), and for small values of T to zero $\left(C_v=\frac{3}{2}R\right)$. As examples of experimental results the following may be quoted:

	approx.
For chlorine at 1,200°C.	$C_v=7{\cdot}0$
For nitrogen at 2,000°C.	$C_v=6{\cdot}7$
For oxygen at 2,000°C.	$C_v=6{\cdot}7$
For hydrogen at 2,000°C.	$C_v=6{\cdot}5$

Chlorine thus shows very nearly the theoretical value 6·98.

Some examples of low-temperature observations are given in the section on gaseous degeneracy.

(iii) *Polyatomic.*—Both theory and experiment are considerably less developed here. Some interesting work has, however, been done by Urey† on the rotational heat of methane. He uses exactly the same method as Reiche, but sets all three moments of inertia equal to one another ($J=2{\cdot}232\times10^{-41}$ grs. cms.^{2}). In the usual way

$$\frac{C_{\text{rot}}}{R}=R\sigma^2\frac{d^2}{d\sigma^2}\log Q$$

where $Q=\sum_1^\infty n^2e^{\sigma n^2}$.

A sketch of Urey's curve is given. Bjerrum, in 1914, contributed a large amount of work on the molecular heats of CO_2, NH_3 and water vapour. No theory corresponding to that existing for diatomic gases has yet been formed. In general, C_v depends more markedly upon temperature for polyatomic gases, but this dependence is very imperfectly known. Before concluding this account of the specific heat of gases two subjects claim brief attention: the effect of pressure upon specific heat and the specific heat of a dissociating gas.

Partington and Shilling, in their book "The Specific Heat of Gases" (Benn, 1924), starting from the usual thermodynamical equation $\left(\frac{\partial C_p}{\partial p}\right)_T=-T\left(\frac{\partial^2V}{\partial T^2}\right)_p$, assume Van de Waal's equation of state, and show that $C_p=ap+b$, so that the relation is linear, which bears out the results of Lussana and Joly. Modern work has not confirmed this. For an ideal gas, $\left(\frac{\partial V}{\partial T}\right)_p$ is constant, so that C_p is independent of the pressure.

---

* Proc. Camb. Phil. Soc., 21, p. 541 (1923).

† Jour. Amer. Chem. Soc., 45, p. 1445 (1923).

In the process of dissociation of a gas which has split up completely or partially into two or more elementary gases, the heat equivalent of the work of dissociation makes a considerable effect upon the apparent specific heat.

Consider the undissociated gas at pressure p. The heat absorbed per molecule for a rise of temperature dT is $C_p dT$.

This quantity $C_p dT$ consists of four parts :

A. The quantity of heat needed to raise the undissociated portion through dT at constant volume. This amounts to $(1-a)C_v dT$ if a is the degree of dissociation and C_v is the molecular heat of the undissociated gas.

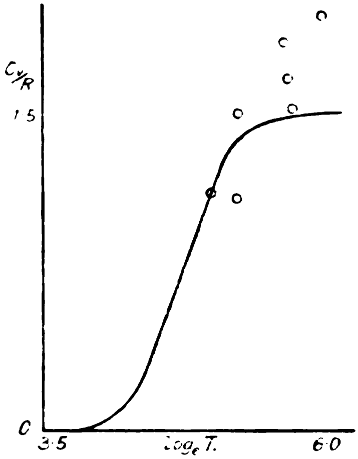


FIG. 3.—THE ROTATIONAL HEAT OF METHANE (UREY).

B. The quantity of heat required to raise the products of dissociation through the same temperature interval. This will be equal to

$$(n_1C_{v1}+n_2C_{v2}\ \ .\ \ .\ \ .\ \ +n_sC_{vs})a\ dT,$$

where n_1 . . . n_s are the number of mols. of each gas for one mol. of the original gas.

C. The heat equivalent of the work of dissociation $p\left(\frac{\partial V}{\partial T}\right)_p$, where V is the volume of the original gas plus that of the products of dissociation.

D. The heat of dissociation (absorbed)$=Q_0\left(\frac{\partial a}{\partial T}\right)_p dT$, assuming that Q_0 is constant.

Thus the total is

$$C_p=(1-a)C_v+a(n_1C_{v1}+n_2C_{v2}\ .\ .\ .\ +n_sC_{vs})+p\left(\frac{\partial V}{\partial T}\right)_p+Q_0\left(\frac{\partial a}{\partial T}\right)_p \quad . \quad . \quad (9)$$

Swart tested this equation for the process $N_2O_4 \rightleftarrows NO_2+NO_2$, and found satisfactory agreement.

(2) CHEMICAL CONSTANTS.

(a) Monatomic Substances.

The thermodynamic vapour-pressure equation for a solid element with monatomic vapour may be written

$$\log p=-\frac{\lambda_0}{RT}+\frac{C_{p\,.\,g}}{R}\log T-\int_0^T\frac{dT}{RT^2}\int_0^T C_k dT+i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where λ_0 is the heat of vapourization at the absolute zero, $C_{p\,.\,g}$ is the molecular heat of the vapour at constant pressure, C_k that of the solid. i is a constant of integration, now generally known as the chemical constant. From statistical considerations, Stern* and Tetrode obtain the expression

$$i=\log\frac{(2\pi m)^{3/2}K^{5/2}}{h^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in the usual notation, which can be put in the simple form

$$\begin{aligned} i &= -i_0+\frac{3}{2}\log M \\ &= -1{\cdot}589+\frac{3}{2}\log M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12) \end{aligned}$$

(M is the molecular weight), taking $h=6{\cdot}55\times10^{-27}$, $N=6{\cdot}06\times10^{23}$, $K=1{\cdot}372\times10^{-16}$. The agreement between the values of i from (10) and (12) is found to be satisfactory for a variety of substances. Egerton† has recently collected together a considerable amount of evidence depending only upon vapour-pressure and specific heat measurements (except in two cases) in favour of the value 1·589 for the constant i_0. He makes no mention of two outstanding exceptions to the Stern-Tetrode formula (11).

Ladenberg and Minkowski‡ have found a discrepancy outside the limit of experimental error for sodium and potassium. From the observed value of i, equation (12) furnishes $i_0=1{\cdot}30$ (from Na) and $i_0=1{\cdot}37$ (from K), instead of 1·589 as theory demands. Schottky§ has questioned whether the quantum weight of the solid is necessarily the same as that of the vapour. This seems to be true for the majority of substances, whereas for sodium and potassium it may be greater for the vapour than for the solid. Another instance of this is monatomic iodine. The simple formula (12) is only true if the weights in the two states are the same. On the other hand, Eucken|| writes: "It is not inconceivable that sodium and potas-

---

* Phys. Zeit., 14, p. 629 (1913). Zeit. für Electrochem., 25, p. 66 (1919).

† Proc. Phys. Soc., 37, p. 75 (1925).

‡ Zeit. für Phys., 8, p. 137 (1921).

§ Phys. Zeit., 22, p. 1 (1921); 23, p. 9 (1922).

|| Ergebnisse der exakten Naturwissenschaften, I, p. 146 (1922).

sium, in the particular temperature interval in which the vapour-pressure curve has been most accurately established, may be partly associated into molecules, whereas the chemical constant has been deduced from the vapour-pressure equation for monatomic substances. The appearance of a band-spectrum in pure potassium vapour indicates the presence of molecules, since band-spectra, according to our present knowledge, are only given out by molecules, not by atoms."

An interesting general point may conveniently be discussed here. Is the chemical constant a special property of the gaseous or of the condensed state? From purely thermodynamical considerations it is difficult to give a satisfactory answer, because we are only dealing with the difference of certain magnitudes, not their absolute values. For instance, the maximum work is a measure of the change of free energy, and in the same way the chemical constant, as it appears in the vapour-pressure equation, is only a measure of the difference between a certain quantity belonging to the solid (or liquid) state, and the corresponding quantity in the gaseous state. It is possible to go a stage further if we take Nernst's Theorem into count in its application to chemical reactions. The chemical constant i here appears in the integrated expression for K_p (the dissociation constant), and, since no condensed phase is supposed to be present, it is reasonable to associate i with the gaseous state. Perhaps the most effective argument is that i (in the vapour-pressure equation) for two allotropic forms of a solid is found to be the same. Although the constitution of the two modifications is different, yet the vapour is the same for both of them. From this it may well be inferred that i is a quantity characteristic of gases.

The opposite point of view has at least one important consideration to recommend it. Equation (11) contains Planck's constant h, which can only be explained on a quantum-theory partition of energy. So far we have only considered the application of such principles to vibrations and rotations, not to translational motion, of which the whole energy in monatomic gases is supposed to consist. From this aspect the tendency would be to ascribe the chemical constant to the condensed state.

(*b*) *Diatomic Substances.*

We have now to consider the two equations:

For the dissociation $X_2 \rightleftarrows 2X$

$$\log K_p = -\frac{Q_0}{4{\cdot}571T} + 1{\cdot}5 \log T - \frac{1}{4{\cdot}571}\int_0^T \frac{dT}{T^2}\int_0^T C_{\text{vib.}}\, dT + 2i_x - i_{x2} \quad . \quad . \quad . \quad (13)$$

where Q_0 is the heat of dissociation at absolute zero.

For the vapour-pressure

$$\log p = -\frac{\lambda_0}{4{\cdot}571T} + 3{\cdot}5 \log T - \frac{1}{4{\cdot}571}\int_0 \frac{dT}{T^2}\int_0^T [C_{\text{vib.}} - C_k]\, dT + i \quad . \quad . \quad . \quad . \quad (14)$$

whilst the statistical work of Ehrenfest and Trkal* leads to the formula

$$i = \log \frac{(2\pi m)^{3/2} \, . \, 8\pi^2 J \, . \, K^{7/2}}{\sigma h^5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

---

* Proc. Amst. Acad., 23, p. 162.

Comparing this with the result for monatomic substances (equation (11)), i (diatomic) is now seen to be a function of the moment of inertia J of the molecule, and a quantity σ, the symmetry number. For the validity of (15) it is necessary that the rotations be fully excited. i as thus defined is the same as Langen's* "chemical constant in the normal state."

The moment of inertia is now known with considerable accuracy from band-spectrum data for a number of diatomic gases, as well as the triatomic molecules CO_2 and H_2O. For triatomic gases J in the formula is replaced by $\sqrt{J_1 J_2 J_3}$, where J_1, J_2, J_3 are the principal moments of inertia. At present a certain amount of discord exists between the values of i (diatomic), as formed thermodynamically, and those calculated on the statistical basis.

In several instances this may be due to the uncertainty which exists in connection with the factor σ. Ehrenfest and Trkal introduce this magnitude into their statistical calculations to allow for the fact that in a symmetrical molecule (say N_2) an exchange of position of the atoms within the molecule is possible, whereas for an unsymmetrical molecule such as CO this is impossible. According to Ehrenfest and Trkal, the phase volumes, if calculated in the ordinary way, would come out to be too great by the factor 2 for diatomic molecules. They therefore subtract log 2, since two exchanges are possible. For a molecule such as CH_4, σ would be equal to 12.

Experiment so far is not sufficiently refined to enable a final judgment to be made as to whether the introduction of σ is correct or not.

The two gases CO and N_2 have almost exactly the same moment of inertia (and the same molecular weight), yet according to Eucken's† latest results, their chemical constants differ by much less than log 2. Cox‡ endeavoured to calculate i for the halogens, but found that the available data were too inexact to enable him to arrive at any definite conclusion with regard to σ. For nitrogen, however, excellent agreement between the statistical and thermodynamical formulæ is obtained on taking $\sigma=2$. The agreement between i (dissociation) and i (vapour-pressure) for the same halogen is not very good, i (vapour-pressure) being about half as great again as i (dissociation). In a recent note§ Cox recalculates i for chlorine, improving the agreement considerably.

The chief cause of error in work of this kind is the uncertainty in the values of Q_0 and λ_0. For instance, there is a difference of some 30 per cent. in the figures for chlorine found by Henglein and by Trautz and Stäckel.

Again, lack of knowledge of possible allotropic changes is responsible for discrepancies of magnitude $q/4{\cdot}571T$, as Cox shows. q is the heat of transformation and T the temperature at which it occurs.

An account of some very detailed work on the constant i is contained in a recent paper by Eucken,‖ where he discusses the gases H_2, N_2, O_2, Cl_2, I_2, NO, CO, HCl, HBr, HI, CO_2, H_2O, NH_3 and CH_4. A new research into the molecular heats of several of these was published at the same time.* Direct data are thereby obtained for the calculation of the integral

---

* Zeit. für Electrochem., 25, p. 28 (1919).
† Zeit. für Phys., 29, p. 1 (1924).
‡ Proc. Camb. Phil. Soc., 21, p. 541 (1923).
§ Loc. cit., 22, p. 491 (1924).
‖ Zeit. für Phys., 29, p. 1 (1924).

$$\int_0^T \frac{dT}{T^2}\int_0^T C_r dT$$

Eucken uses the figures he obtains for i to deduce the moment of inertia J_i from formula (15), omitting σ, and compares this with the value $J_{\text{opt.}}$ obtained from the spectra. The differences are marked and show little regularity. Thus for O_2, NO, HCl, HBr, HI, $J_i > J_{\text{opt.}}$, whereas for H_2, N_2, CO, CO_2, H_2O, he finds the reverse. Up to the time of writing, no explanation of these irrelguarities has been suggested.

(3) GASEOUS DEGENERATION.

In the portion of this paper dealing with specific heats we have considered the falling-off, according to the quantum theory, of the rotational and vibrational molecular heats of diatomic gases with decreasing temperature. The experimental fact there mentioned was that in hydrogen (below 60° absolute) the molecular heat C_v resembled that of a monatomic gas in having the value $\frac{3}{2}R$, corresponding to translational energy alone. Tetrode† and others have attempted to apply the quantum theory to translations. At present the whole basis is very insecure. The method is to consider the thermal motions in a gas divided up into a spectrum of natural frequencies. The energy is then distributed among the natural frequencies according to the usual equation $\overline{U}=\frac{\varepsilon}{e^{\frac{\varepsilon}{KT}}-1}$.

Planck‡ and Scherrer§ apply the quantum rules directly to the individual atoms, and show that their velocity and energy of translation can only acquire discrete values. Eucken|| has measured the molecular heats of hydrogen and helium at high pressures and at very low temperatures.

He finds that the molecular heat falls even below $\frac{3}{2}R$. Thus, for hydrogen

$T=29{\cdot}6°$ abs.	$C_v=3{\cdot}20$
$24{\cdot}0°$	$3{\cdot}02$
$21{\cdot}2°$	$2{\cdot}78$
$18{\cdot}6°$	$2{\cdot}70$

The reading at 29·6° when recalculated by Berthelot's equation yields approximately $C_v=2{\cdot}98$, so that at lower temperatures C_v is even smaller than that of a perfect gas where the whole energy is translational.

Again, the greater the compression the lower the value of C_v for a given temperature.

The effect is sketched in a graph for two volumes, ($V_1 > V_2$).

---

* Zeit. für Phys. Chem., 112, p. 467 (1924).

† Phys. Zeit., 14, p. 212 (1913). Ann. der Phys., 38, p. 434 (1912).

‡ Berl. Ber., p. 653 (1916).

§ Göttingen Nachr., July 8, 1916.

|| Ber. Deut. Phys. Ges., 18, p. 4 (1916).

Nernst discusses this " degeneration " from the ideal gaseous state.

He postulates a special kind of rotation of the molecule not caused by collisions, but due to the transformation of the translational energy, presumably *per se,* into " rotational " energy. It is only necessary to remember that the frequency of the true molecular rotations existing at higher temperatures must be very much greater than that associated with this " degenerate rotation " to see how very speculative Nernst's ideas are.

If these " rotations " are to be quantized we must write for the energy in the degenerate state

$$U=\frac{3}{2}R\frac{\beta\nu}{e^{\beta/T}-1},$$

so that C_v tends to zero for $T=0$. Support for some such conception is afforded by Eucken's observations, but it is difficult to follow Nernst in his view of degenerate rotation. It may be mentioned here that one of the chief points of the theory of gaseous degeneracy lies in the possibility which springs from it of applying the Nernst Heat Theorem directly to gases.

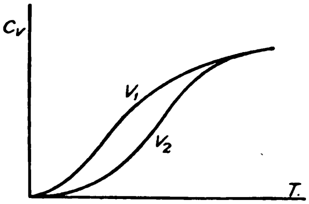


FIG. 4. THE "DEGENERATION" OF HYDROGEN (EUCKEN).

Since the details of this are hardly germane to the purpose of the present essay, it will not be considered further.

Assuming, however, that such an application is justifiable, Nernst* deduces on a degeneracy basis a value for the chemical constant of monatomic gases. He finds

$$i=\log\frac{(4\pi m)^{3/2}k^{5/2}}{eh^3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

compared with Ehrenfest's and Trkal's

$$i=\log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}$$

The ratio $$\frac{(4\pi)^{3/2}/e}{(2\pi)^{3/2}}=1{\cdot}015.$$

Experiment is hardly accurate enough yet to make a decision between the two.

For the sake of completeness, mention should be made of Lindemann's† adverse criticism of the whole theory of degeneracy in gases.

---

[*] Grundlagen des neuen Wärmesatzes (1918).

[†] Phil. Mag., 39, p. 21 (1920).

His argument is based almost entirely upon dimensional considerations. Rejecting degeneracy, he shows that if $C_p=\frac{5}{2}R$ down to the absolute zero, it might be possible to link up the chemical constant with radiation theory.

The most recent work on the subject is that of Bennewitz,* who sets out to find the general equation of state of an (ideal) degenerate gas, which shall not conflict with the Nernst degeneracy equation of energy

$$U=\frac{3}{2}RT\cdot\frac{1}{2}x\cdot\frac{e^x+1}{e^x-1}\quad\ldots\ldots\ldots\ldots\quad(17)$$

$$\left[x=\frac{\beta\nu}{T}=\frac{h^2N^{\frac{2}{3}}}{4\pi mk}\cdot\frac{1}{TV^{2/3}},\ V=\text{molar volume}\right]$$

and which satisfies

(*a*) The 1st and 2nd laws of Thermodynamics,

(*b*) The classical equation $pv=\frac{2}{3}U$ (for ideal gases),

(*c*) The Nernst Heat Theorem,

(*d*) The condition $\left(\psi+T\frac{d\psi}{dT}\right)_{T=0}=0$ (ψ defined as below).

The equations found are

$$U=\frac{3}{2}RT\psi\quad\ldots\ldots\ldots\ldots\quad(18)$$

$$pv=RT\psi\quad\ldots\ldots\ldots\ldots\quad(19)$$

where ψ is a function of $\left(\frac{\text{constant}}{TV^{2/3}}\right)=f(x)$.

As a result, C_v is no longer equal to $\frac{3}{2}R$ for an ideal monatomic gas, but to

$$\frac{3}{2}R(1-a),\text{ where }a=\frac{x}{\psi}\cdot\frac{d\psi}{dx}.$$

Similarly C_p becomes $\frac{5}{2}R\,\frac{1-a}{1+\frac{2}{3}a}$, so that the difference of the specific heats is no longer independent of the temperature and equal to R as on the classical theory, but to $R\,\frac{(1-a)^2}{1+\frac{2}{3}a}$. Also the ratio $\gamma\left(=\frac{C_p}{C_v}\right)$ no longer has the value $\frac{5}{3}$, but involves the degeneracy function ψ, and becomes equal to $\frac{5}{3}\,\frac{1}{1+\frac{2}{3}a}$. Bennewitz discusses the limiting cases $T=0$ and $T=\infty$ in connexion with the problem of the existence of a zero-point energy.

---

* Zeit. für Phys. Chem., 110, p. 725 (1924).

The results may be tabulated for convenience :—

——	$T=0$	$T=0$	——	$T=\infty$	$T=\infty$
	Classical.	Deg.		Classical.	Deg.
C_v	$\frac{3}{2}R$	0	C_v	$\frac{3}{2}R$	$\frac{3}{2}R$
C_p	$\frac{5}{2}R$	0	C_p	$\frac{5}{2}R$	$\frac{5}{2}R$
$C_p/C_v=\gamma$	$\frac{5}{3}$	1	$C_p/C_v=\gamma$	$\frac{5}{3}$	$\frac{5}{3}$
C_p-C_v	R	0	C_p-C_v	R	R

Thus the degenerate values pass over into the classical values at high temperatures In this connexion the author discusses a kind of Correspondence Principle analogous to that of Böhr in the quantum theory, in which " degenerate " thermodynamics can be considered to become classical for large values of T.

According to Bennewitz, the equation for the chemical constant is

$$i=\log R\psi(0)-\frac{3}{2}\log C-\frac{5}{2}+\frac{1}{R\psi(0)}\int^{0}\log x\,\frac{dC_v}{dx}\,dx \quad . \; . \; . \; . \; . \; . \; . \quad (20)$$

It is interesting to verify that this reduces to Nernst's expression (17) for ordinary (high) temperatures.

For T large $\psi(0)=1$

$$C=\frac{h^2N^{2/3}}{4\pi mk}$$

$$\int^{0}\log x\,\frac{dC_v}{dx}\,dx=\frac{3}{2}R[\log x]_0+\frac{3}{2}R\left[\frac{xe^x}{e^x-1}\right]-\frac{3}{2}R\,[\log e^x-1]^{0}_{\infty}=\frac{3}{2}R$$

$$\text{Thus } i=\log Nk-\frac{3}{2}\log\,(h^2N^{2/3}/4\pi mk)-\frac{5}{2}+\frac{3}{2}=\log\frac{(4\pi m)^{3/2}k^{5/2}}{eh^3}$$

as already given (equation (16)).

There remains a recent Paper of Eucken's* to be considered. He establishes the thermodynamical relations for chemical equilibrium in twenty-one typical homogeneous and heterogeneous reactions, and obtains the constant i_K corresponding to i in the vapour-pressure equation.

The results are not consistent, but the point of interest here is that the equation $i_K=\Sigma i$, as demanded by Nernst's Theorem, is not satisfied.

DISCUSSION.

Capt. A. C. G. EGERTON : Mr. Rawlins has given a very interesting résumé of the position of theory in respect of the specific heat of the solid and gaseous states. He mentions that in my Paper to the Physical Society last year I omitted to mention the work of Ladenburg and Minkowski on the vapour pressure of sodium and potassium, and the irregular values of the chemical constants of those metals. The measurements on which they base those values are, however, not direct vapour-pressure measurements. We have made a series of measurements on the vapour pressures of sodium and potassium, and although the work is not quite completed, the evidence so far is that there is nothing irregular in the value of the constants for these two metals.

---

* Zeit. für Phys., 29, p. 36 (1924).

Another point of interest, I think, in connection perhaps with difficulties respecting theories of specific heat of gases is the existence of absorption bands due to the temporary formation of diatomic molecules in vapours where, from ratio of specific heat measurements and also vapour-pressure measurements, there is no evidence of any but monatomic molecules. Franck and others have investigated this matter in the case of mercury.

Dr. D. OWEN said he thought it a very good thing that the Society should have Papers of the present kind from time to time, in spite of the great difficulty of the subject matter, which is somewhat strange to the majority of experimental physicists. Great Britain has of late tended to lag behind continental countries in mathematical physics, and therefore the school with which Capt. Egerton is associated at Oxford, and that which the author is forming at Cambridge, are of great importance, and deserve the best wishes of British physicists. Dr. Owen added that the conception of the chemical constant i merely as a constant of integration is a little unsatisfying. Is it possible to form a more concrete conception of it ?

AUTHOR'S reply : I am grateful to Captain Egerton for his remarks. It is satisfactory to learn that recent work tends to show that the behaviour of Na and K is normal with respect to the constant i_0. This naturally is to be welcomed as rendering it needless to make somewhat arbitrary assumptions as to the relative quantum weights of solid and vapour.

In reply to Dr. Owen : While sympathizing with his wish for a more physical picture of i, may I venture to suggest that this quantity suffers from the same inherent kind of " aloofness " as entropy ; which latter only received a satisfactory physical basis at the hands of Carathéodory (Math. Ann. 61, 355, 1909) ? The views of Prof. Lindemann (referred to in my Paper) are very suggestive.

Dr. ALLAN FERGUSON (communicated) : I should like to express my thanks to Mr. Rawlins for his very clear summarising of this new knowledge. Very many of us have felt that the light cast upon physico-chemical problems by the chemical constant has been rather less than that of a farthing candle. Mr. Rawlins' efforts have considerably increased the intensity of that illumination.

My own interest in the chemical constant is indirect. As Mr. Rawlins has pointed out, the value of Q_0 is subject to considerable error. Van't Hoff's reaction isochore

$$\frac{d(\log K)}{dT}=\frac{Q}{RT^2}$$

cannot be integrated until we know Q as a function of T. Van't Hoff's equation has a rational basis, but no such basis has been suggested for the *velocity* constants k_1 and k_2 for, say a bimolecular reaction. Arrhenius has put forward an empirical relation

$$\frac{d(\log k)}{dT}=\frac{a}{RT^2}$$

where a is constant. This leads to

$$\log k=A-\frac{B}{T},$$

but a plot of $1/T$ against $\log k$ shows in general distinct curvature. I am at present investigating other relations between $\log k$ and T, some of which seem promising. These relations, together with the known relation between K, k_1 and k_2, suffice to give Q as a function of T having at least a semi-rational basis. These relations may serve to test the usual " Planckian " equation for Q,

$$Q=Q_0+\frac{h\nu_0}{k}R\frac{e^{-\frac{h\nu_0}{kT}}}{1-e^{-\frac{h\nu_0}{kT}}}-3T,$$

at ordinary temperatures, and possibly to form a basis for reliable values of Q_0, although extrapolations are always doubtful.

XXII.—ON THE "HYPERBOLA" METHOD FOR THE MEASUREMENT OF SURFACE TENSIONS.

By A. FERGUSON, *M.A.*, *D.Sc.*, and I. VOGEL, *B.Sc.*

ABSTRACT.

When a liquid lies between two plates inclined to one another at a small angle its surface has a hyperbolic section, from measurement of which the surface tension can be calculated. The method has long been known, but has recently been improved by Grünmach. Errors arise, however, from the difficulty of determining the horizontal and vertical axes of co-ordinates, and according to the present Paper this difficulty is met by plotting two linearly related functions of the observations, the surface tension being deduced from the co-ordinates of the resulting mean straight line and the angle between the plates. The latter may be measured either directly or by calibration with a liquid of known surface tension.

THE surface tension of a liquid may be deduced from measurements made on the curve assumed by a liquid after rising between two vertical plates inclined to each other at a small angle. The values so obtained are not usually very exact, and the method, for a good many years past, has been relegated to the comparative obscurity of a laboratory illustration of the principles of surface tension.

In a series of Papers,* of which the principal one is entitled " Uber ein *neuen* Plattenapparat zur Bestimmung von Kapillaritätskonstanten nach der Steighöhenmethode," Grünmach has introduced into the method certain modifications which are intended to simplify its technique and increase its accuracy. The word " new " in the title just given may presumably be used in virtue of these modifications, but the method itself is of very respectable antiquity. It was described, and the hyperbolic nature of the curve was recognised, by Brook Taylor† and by Hauksbee‡ in 1712-13. The apparatus and the curve are admirably figured in s' Gravesande's§ " Mathematical Elements of Natural Philosophy," and the proof given by Musschenbroek|| may be quoted even now as one of the most compact proofs of the nature of the capillary curve.

Apart from any small corrections concerning the nature of the capillary surface, the manner in which the hyperbolic nature of the surface-curve depends on the smallness of the angle between the plates is easily investigated. Thus, assuming a

---

* Grünmach, Physik. Zeitschr., 11, 980 (1910). Grünmach, Zeitschr. Instrumentenk., 30, 366 (1910). Grünmach and Bein, Zeitschr. Instrumentenk., 39, 195 (1919).

† Phil. Trans., 27, 538 (1712).

‡ Phil. Trans., 28, 151 and 153 (1713).

§ English translation by Desaguliers, 4th edition (1731).

|| Introductio ad Philosophiam Naturalem, Tom. 1, p. 376 (1762). " Si ambo specula plana, ad solum perpendicularia, uno latere jungantur, ut se contingant : opposito latere distiterint, angulumque forment, haec imposita Aquae, eam altius attollent, in locis, quibus specula sint propriora ; minus ubi specula plus distant ; elevatae aquae inter specula superficies formabit curvam, Hyperbolam, cujus Asymptotae erint speculi latera *CD*, *DE* ; est enim *Da* ad *Db* ut distantia speculorum *aa'* ad *bb'* : sed est altidudo *Bb* ad *Aa* in ratione inversa distantiorum in his locis ; sive est uti *Da* ad *Db* : adeoque erit $Da \times Aa = Db \times Bb$. Quae est proprietas Hyperbolae." (*See* Fig. 1).

zero-contact angle with glass (γ being the surface tension of the liquid, and φ the angle between the plates), we have for the vertical component of the tensions along AB and $A'B'$ the value $2\gamma ds \cos\theta$ or $2\gamma dx$. The difference of the vertical components on AA' and BB' is

$$\gamma\varphi dx \,.\, \frac{d}{dx}(x\sin\theta).$$

Hence, if the area of the base is δA, we have

$$2\gamma\delta x = g\rho y\delta A + \gamma\varphi\frac{d}{dx}(x\sin\theta)\delta x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

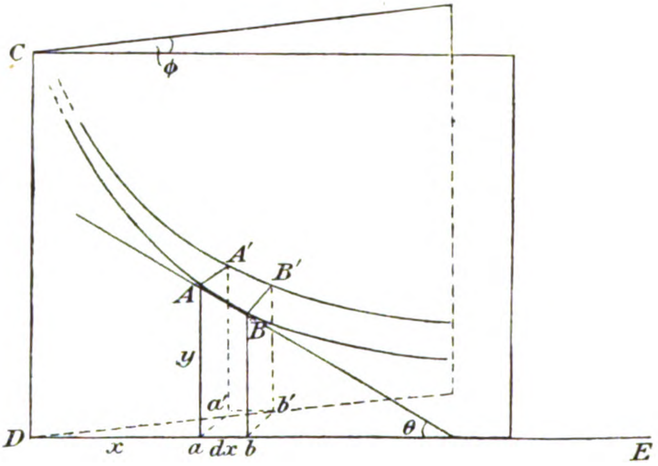


FIG. 1.

Including terms of the order φ^2, we have for δA

$$\delta A = \varphi x\delta x,$$

and (1) then becomes

$$2\gamma = g\rho\varphi xy + \gamma\varphi\frac{d}{dx}(x\sin\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Approximately

$$xy = \frac{2\gamma}{g\rho\varphi} = K \text{ (say)};$$

and hence

$$\tan\theta = -\frac{dy}{dx} = \frac{K}{x^2};$$

or, taking the positive sign for $\sin\theta$,

$$\sin\theta = \frac{K}{\sqrt{K^2+x^4}}$$

This gives

$$\frac{d}{dx}(x\sin\theta)=y\cdot\frac{y^2-x^2}{(y^2+x^2)^{3/2}}$$

which value, substituted in (2), together with the approximate value

$$\gamma=\frac{g\rho\varphi xy}{2}$$

leads immediately to the equation

$$2a^2\equiv\frac{2\gamma}{g\rho}=\varphi xy\left\{1+\frac{\varphi}{2}\cdot y\cdot\frac{y^2-x^2}{(y^2+x^2)^{3/2}}\right\}\quad\ldots\ldots\quad(3)$$

Equation (3) shows clearly the conditions under which the hyperbolic formula is valid. If φ be sufficiently small, we have

$$xy=\frac{2a^2}{\varphi}=K\quad\ldots\ldots\quad(4)$$

which is the relation usually employed. If, however, we find a systematic variation in K, a plot of two new variables (X, Y), given by

$$xy=Y \text{ and } xy^2\cdot\frac{y^2-x^2}{(y^2+x^2)^{3/2}}=X,$$

should yield a straight line

$$Y+\frac{\varphi}{2}X=\frac{2a^2}{\varphi}\quad\ldots\ldots\quad(5)$$

whose slope and intercept determine a^2 and φ. In all ordinary instances equation (4) is sufficiently exact.

In Grünmach's earlier apparatus, the values of x and y are determined, by means of a kathetometer, relative to the axes DE and DC of Fig. 1. The "constant" xy is not at all constant, but in certain instances shows indications of the systematic variation just mentioned. Table I below, which is taken from Grünmach's Paper sufficiently illustrates this point.

TABLE I.

Pure oleic acid. Curve 1.			Temp. 20°C. Curve 4.		
x	y	xy	x	y	xy
25	11·6	290	35	19·5	684·3
30	9·7	291	40	17·1	684
35	8·5	297·5	45	15·1	679·5
		——	50	13·7	685
	Mean ...	293	55	12·4	682
			60	11·6	696
			65	10·7	695·5
			70	10·0	700
					——
				Mean ...	688·3

Nevertheless, Grünmach considers himself justified in taking a mean value of the constant and calculating y from a formula equivalent to the simple formula (4). In his later apparatus he photographs a series of confocal hyperbolæ on one of the plates, and adjusts the angle between the plates until the curve of the liquid surface coincides, as nearly as may be, with one of the curves.

The difficulties attendant upon the practice of either of these methods are apparent. It is not easy to determine accurately the line about which the plate rotates, and, what is of primary importance, it is difficult to determine directly the position of the axes *DC* and *DE*, to which the values of the co-ordinates are to be referred.

The modification of the method used by the present writers in great measure evades these difficulties. Two selected pieces of plate glass are cut as accurately as possible into rectangular shape, and their edges polished off smoothly, so that their distance apart can be accurately measured. They are clamped together so as to make a small angle with each other by inserting between their upper portions a wedge-shaped piece of brass which is smoothed off to an appropriate small angle. The wedge used was about 1 mm. thick at its base, and was smoothed off to such an angle that the plates, about 12 cms. wide, were in contact along one pair of vertical edges when the base of the wedge was flush with the other pair of edges. The plates were secured in position by stout rubber bands and by bull-dog clips, which could always be placed in the same position with reference to fiducial lines ruled on the plates. In the earlier recorded experiments the two plates were held at the top by a simple clamp, which permitted of their adjustment so that the line of contact might be made accurately vertical by comparison with a plumb-line. The amount of separation of the plates could be altered slightly by altering the pressure of the clamp, and in the later comparative experiments the upper edge of one plate was adjusted to be about 1 cm. higher than the upper edge of the other, and this projecting portion of the back plate was then fixed in the clamp. The plates having been cleaned with chromic acid, washed, dried and finally polished with a clean silk duster, are set up in the manner described and immersed in a vessel containing the liquid under experiment. The vessel is raised and lowered several times, and the liquid between the plates finally settles into a beautifully smooth curve, the co-ordinates of which may easily be read off. We employ for this purpose an x-y microscope set, with its lines of travel accurately horizontal and vertical.

As we have previously mentioned, a serious defect of the method lies in the difficulty of accurately determining the axes. This remark applies specially to the horizontal axis. The difficulty may be evaded by measuring the y co-ordinate from *any* horizontal axis, the values of x being measured from the line of junction of the plates. We then have, in place of (4),

$$x(y+k)=K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that a plot of xy as Y against x yields a straight line whose intercepts give the desired constant K. But it is not necessary to know the position of either x or y

axis, provided that we measure our values of x and y referred to any axes parallel to DC and DE (Fig. 1). We then have

$$(x+h)(y+k)=K \qquad \ldots\ldots\ldots\ldots \qquad (7)$$

and easy graphical methods are known by which h and k may be determined.* Thus, if we take any point (x_0, y_0) *on the curve* as a new origin, so that $X=x-x_0$, $Y=y-y_0$, a plot of Y against Y/X as x gives a straight line

$$Y=-(x_0+h)Y/X-(y_0+k) \qquad \ldots\ldots\ldots \qquad (8)$$

and the slope and intercept of (8) give h and k. These being known, every value of x and y gives by (7) a value of K, and the mean of these values so obtained is used in computing γ from (4).

The liquids experimented on were water, benzene and toluene. These were purified as follows :—

Water.

The water was siphoned from the middle of a tank containing about 100 litres of distilled water.

Benzene.

Pure recrystallised benzene of commerce, "benzene cryst," was first fractionated, the portion collected distilling between 0·1°C. It was free from thiophene by repeated shaking with concentrated sulphuric acid, was washed twice with water, twice with sodium carbonate solution, and twice again with water ; it was then dried over calcium chloride, refluxed over sodium for several hours, and fractionated over sodium. The fraction collected distilled within 0·05°C.

Toluene.

Commercially pure toluene was treated much as described above under the heading "Benzene." The fraction finally collected after distillation over sodium distilled within 0·1°C.

The specific gravities of the pure liquids as determined by means of the specific gravity bottle were

Benzene $\rho_4^{20\cdot5}=0\cdot8772$

Toluene $\rho_4^{20\cdot5}=0\cdot8643.$

Two methods of experimenting were employed by us. In the first instance, the method was used as an absolute one. After determining the constant K as described above, the mean distance apart of the edges of the plates was measured by means of the scale in the eye-piece of a travelling microscope, which permitted of readings being taken to 0·0025 mms. This length divided by the length of either plate gave the angular separation of the plates, and γ follows at once from equation (4). On the other hand, it may happen that a laboratory is unprovided with the means for measuring φ to the order of accuracy necessary. In these circumstances, φ may be determined if we perform a preliminary experiment with a liquid (benzene or water) whose surface tension may be assumed known.

---

* See Running "Empirical Formulas," p. 53 (1917).

Table II below shows in detail the result of an experiment made on distilled water :—

TABLE II.—*Water—Experiment* 1.

x cms.	y cms.	X	Y	Y/X	$(x+h)$	$(y+k)$	$(x+h)\,(y+k)$
14·533	14·744	4·533	9·271	2·045	−1·306	11·941	15·59
14·000	11·257	4·000	5·784	1·446	−1·839	8·454	15·55
13,500	9·404	3·500	3·931	1·123	−2·339	6·601	15·44
13·000	8·269	3·000	2·796	0·932	−2·839	5·466	15·52
12·500	7·419	2·500	1·946	0·778	−3·339	4·616	15·41
12·000	6·873	2·000	1·400	0·700	−3·839	4·070	15·62
11·500	6·389	1·500	0·916	0·611	−4·339	3·586	15·56
11·000	6·029	1·000	0·536	0·536	−4·839	3·226	15·61
10·500	5·716	0·500	0·243	0·486	−5·339	2·913	15·55
10·000	5·473	0·000	0·000	0·000	−5·839	2·670	15·59
9·500	5·256	−0·500	−0·217	0·434	−6·339	2·453	15·55
9·000	5·068	−1·000	−0·405	0·405	−6·839	2·265	15·49
8·500	4·921	−1·500	−0·552	0·368	−7·339	2·118	15·54
8·000	4·779	−2·000	−0·694	0·347	−7·839	1·976	15·49
7·500	4·675	−2·500	−0·798	0·319	−8·339	1·872	15·61
7·000	4·561	−3·000	−0·912	0·304	−8·839	1·758	15·54
6·500	4·451	−3·500	−1·022	0·292	−9·339	1·648	15·39
6·000	4·377	−4·000	−1·096	0·274	−9·839	1·574	15·49
5·500	4·310	−4·500	−1·163	0·258	−10·339	1·507	15·58
5·000	4·248	−5·000	−1·225	0·245	−10·839	1·445	15·63
						Mean ...	15·54

The graph of Y/X against X gives the curve of Fig. 2.

The constants of this line are

$$m=5{\cdot}839,\quad c=2{\cdot}670\ ;$$

whence

$$h=-15{\cdot}84,\quad k=-2{\cdot}803.$$

The mean value of K is 15·54, and by measurement with the microscope

$$\varphi=0{\cdot}1190\div 12{\cdot}40.$$

Hence, substituting in (4), we have at a temperature of 14·1 C.

$$\gamma=73{\cdot}15 \text{ dyne cm.}^{-1}.$$

[In succeeding records we restrict ourselves to giving the separate values of the constant only ; it is the magnitude of the variation of this quantity which serves initially as a criterion of the trustworthiness of the method.]

Water—Experiment 2.

Values of K—

19·03, 19·14, 19·04, 18·95, 19·12, 19·03, 19·08, 19·02, 19·07, 19·03, 19·05.

Mean 19·05.

$$\varphi=0{\cdot}09750\div 12{\cdot}62.$$

Temp. 23·9°C.

$$\gamma=72{\cdot}19 \text{ dyne cm.}^{-1}.$$

***Water—Experiment* 3.**

Values of K—

20·31, 20·56, 20·10, 20·60, 20·06, 20·34, 19·81, 20·25, 19·88, 20·05, 19·83, 20·06, 19·65, 19·83, 19·64, 19·87.

Mean 20·05.

$\varphi = 0{\cdot}09425 \div 12{\cdot}62.$

Temp. 14·9°C.

$\gamma = 73{\cdot}45$ dyne cm.$^{-1}$.

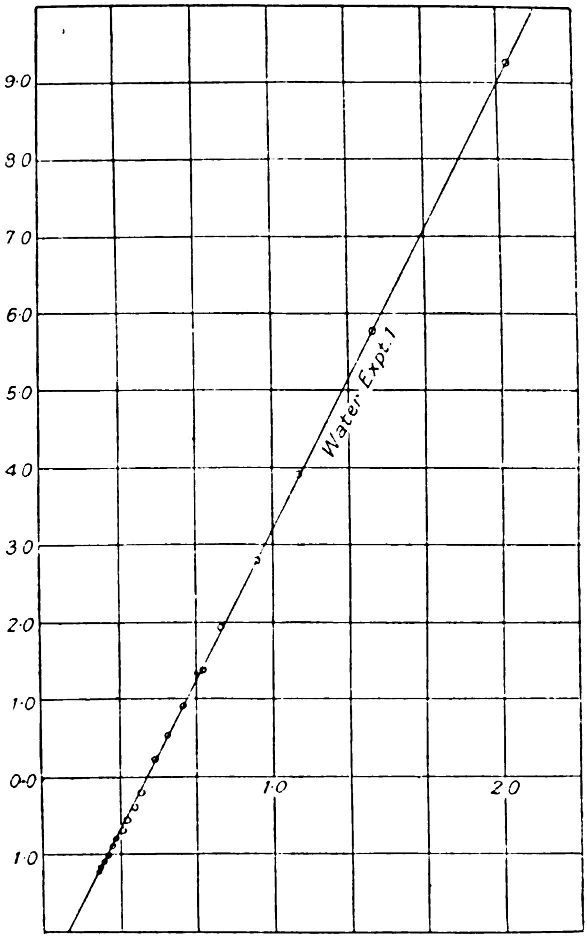


FIG. 2.

Benzene—Experiment 1.

Values of *K*—

8·965, 8·965, 9·062, 9·052, 9·063, 9·019, 8·965, 9·033, 9·022, 9·108, 9·122, 9·152, 9·107, 9,062, 9·170, 9·080.

Mean 9·059.

$\varphi=0{\cdot}09500\div12{\cdot}62.$

Temp. 16·3°C.

$\gamma=29{\cdot}34$ dyne cm.$^{-1}$.

Benzene—Experiment 2.

Values of *K*—

8·003, 8·219, 8·263, 8·241, 8·242, 8·296, 8·168, 8·274, 8·248, 8·238, 8·287, 8·249, 8·177, 8·211, 8·266.

Mean 8·225.

$\varphi=0{\cdot}1030\div12{\cdot}40.$

Temp. 16·0°C.

$\gamma=29{\cdot}39$ dyne cm.$^{-1}$.

Benzene—Experiment 3.

Values of *K*—

8·381, 8·297, 8·339, 8·337, 8·372, 8·371, 8·299, 8·361, 8·339, 8·396, 8·327, 8·375.

Mean 8·348.

$\varphi=0{\cdot}1010\div12{\cdot}40.$

Temp. 15·4°C.

$\gamma=29{\cdot}26$ dyne cm.$^{-1}$.

Collecting these results and assuming a temperature coefficient of 0·15 dyne cm.$^{-1}$ (degree Cent.)$^{-1}$ for water, and 0·13 dyne cm.$^{-1}$ (degree Cent.)$^{-1}$ for benzene, we find values for γ in fair agreement with those found by other methods.

TABLE III.

Water.			Benzene.		
Temp. θ	γ_θ	γ_{15°	Temp.	γ_θ	γ_{20°
14·1	73·15	73·01	16·3	29·34	28·85
23·9	72·19	73·53	16·0	29·39	28·87
14·9	73·45	73·43	15·4	29·26	28·66
	Mean ...	$\gamma_{15^\circ}=73{\cdot}32$		Mean ...	$\gamma_{20^\circ}=28{\cdot}74$

We now turn to the results obtained by the comparative method. Benzene was used as the standard liquid, the surface tension of benzene being taken as 28·88 dyne cm.$^{-1}$ at 20·0°C.* The values of *h* and *k* being determined as described we find the values given below for the constant *K*.

---

* Richards and Carver, J. Amer. Chem. Soc., 43, 827 (1921).

Benzene—Experiment 4.

Values of *K*—

10·28, 10·15, 10·19, 10·15, 10·18, 10·16, 10·12, 10·15, 10·19, 10·02, 10·13, 10·00, 10·17, 10·17, 10·21.

Mean 10·15.

This leads at once from equation (4) to the value

$$\varphi=6{\cdot}612\times10^{-3}.$$

The results for three experiments with toluene are given below. The plates were taken down, cleaned, dried and reassembled between each experiment.

Experiment 1.

Values of *K*—

10·09, 10·05, 10·04, 10·06, 10·06, 10·05, 10·08, 10·10, 10·04, 10·12, 10·17, 9·98, 10·05, 10·14, 10·06, 10·00.

Mean 10·07.

$$\varphi=6{\cdot}612\times10^{-3}.$$

Temp. 21·8°C.

$$\gamma=28{\cdot}23 \text{ dyne cm.}^{-1}.$$

Experiment 2.

Values of *K*—

10·02, 9·845, 9·982, 9·975, 9·974, 9·941, 9·977, 10·02, 9·885, 9·763, 9·916, 9·898, 9·930, 9·945, 9·970, 9·868, 9·981.

Mean 9·935.

$$\varphi=6{\cdot}612\times10^{-3}.$$

Temp. 23·8°C.

$$\gamma=27{\cdot}85 \text{ dyne cm.}^{-1}.$$

Experiment 3.

Values of *K*—

10·02, 9·936, 9·946, 9·939, 9·980, 9·983, 9·987, 9·932, 9·894, 9·987, 9·926, 10·10, 10·15, 9·979, 10·18.

Mean 9·996.

$$\varphi=6{\cdot}612\times10^{-3}.$$

Temp. 20·2°C.

$$\gamma=28{\cdot}02 \text{ dyne cm.}^{-1}.$$

The results for toluene and their reduction to γ_{20° by means of a known temperature coefficient are exhibited in Table IV.

TABLE IV.

Temperature coefficient assumed = 0·15 dyne cm.$^{-1}$ (degree Cent.)$^{-1}$.

Temp. θ	γ_θ	γ_{20°
21·8	28·23	28·50
23·8	27·85	28·42
20·2	28·02	27·99
	Mean	$\gamma_{20^\circ}=28{\cdot}30$

The mean value given above is in fair agreement with the value 28·43 dyne cm.$^{-1}$ obtained by Richards and Carver. A number of the straight lines from which the values of *h* and *k* are determined are shown in Fig. 3, and it will be seen that they are very accurately rectilinear, the coefficient being determined without any trace of ambiguity.

It is no easy matter to obtain consistent surface tension measurements in a London atmosphere, especially when the method employed involves the handling and exposure of large quantities of liquid. Some of our experiments, notably those with water, gave values of *K* which in any one experiment were perfectly self-consistent, but which gave low and irregular values for the surface tension. These irregularities are to be attributed to atmospheric impurities, for it is the experience

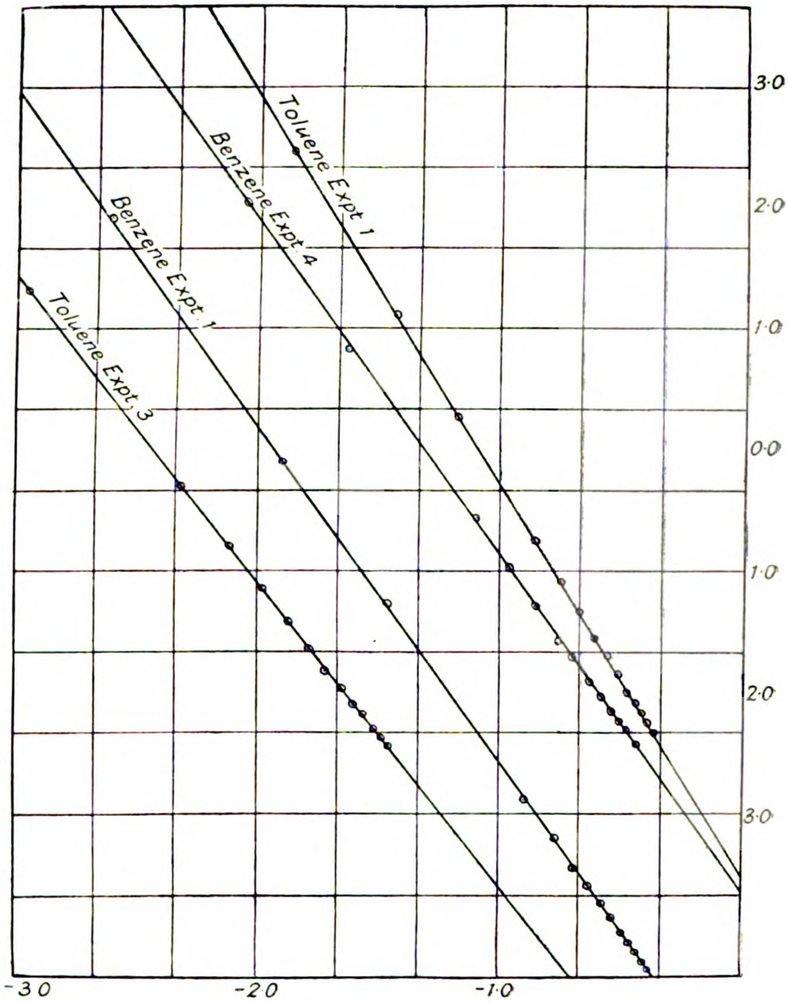


FIG. 3.

of one of us that the method, given in its primitive form as a laboratory experiment, can be depended to give values correct to about 1 per cent. in a pure atmosphere.

When the observations are reduced in this manner, we feel that the technique of the method is considerably more accurate than the technique employed by Grünmach. It has one of the limitations of the capillary rise method, in that it assumes that the liquids under experiment have a zero contact angle. Moreover, the gain of precision which this method of reduction entails is accompanied by a corresponding increase in the time spent. A good deal of this time and labour might be saved if the front plate be ruled with one horizontal and a series of vertical lines exactly 1 cm. apart, the vertical lines being marked off in millimetres. The instrument then becomes one which makes very little demand on the resources of a technical laboratory—a point of some importance in technological practice—the only accessories needed being a hand lens for reading off the y-co-ordinates to the nearest tenth of a millimetre, and a sample of some liquid of known surface tension for standardisation.

DISCUSSION.

Dr. J. H. VINCENT suggested that in addition to avoiding errors of displacement in the co-ordinate axes, the method might yield a correction for errors in the verticality of the line of intersection of the plates.

Mr. T. SMITH said that in introducing his Paper the author had referred to lens-system formulæ which could be transformed so as to yield linear graphs, and had suggested that the co-ordinates of the resulting mean straight lines would give average results for the observations on which they were based. It must be remembered, however, that geometrical optics represents only an approximation to the physical facts, and that the values obtained in different regions of a range of observations have very different probabilities of error. In practice the mean adopted must be a weighted mean, which is not provided by the linear-graph method.

XXIII.—THE APPLICATION OF RADIOGRAPHY TO THE STUDY OF CAPILLARITY.

By E. A. Owen, *M.A., D.Sc.*, and A. F. Dufton, *M.A., D.I.C.*, Physics Department, National Physical Laboratory.

Abstract.

The X-ray shadow of a tube has previously been used for determining the diameter of the bore. The present investigation was designed to test the suitability of a similar method for capillarity measurements, and observations were made of the rise of mercury in copper and steel tubes and between vertical copper plates. The results were satisfactory.

THE radiographic method has been successfully employed for the measurement of the internal diameters of tubes.[*] It occurred to the authors that the method might prove useful for the study of problems in capillarity and a few experiments, a brief account of which is given in this Paper, were carried out to investigate it from this point of view.

Avogadro[†] determined the capillary constant for mercury by measuring the rise in a copper tube 2·80 mm. in diameter, well amalgamated in the interior, and found it to be 5·56 sq. millimetres. This value is lower than those determined subsequently by other methods.

In repeating this experiment, two tubes having internal diameters of 1·62 mm. and 2·09 mm. respectively were employed. The tubes were well amalgamated and thoroughly cleaned before being introduced into a trough of distilled mercury, in which they were held when the radiograph shown in Fig. 1 was taken. The X-ray bulb used for the work had a tungsten anticathode and was operated at 2 milliamperes and 120 kilovolts. The tubes were situated a metre away from the X-ray bulb with the photographic plate or film fixed close behind them. The exposure under these conditions was about three minutes.

The values of the surface tension of mercury at 17°C. (room temperature) deduced from the measurement of the radiograph are included in Table I. The two tubes gave quite consistent results.

Table I.

Diameter of tube (d).	Capillary rise (h).	$a^2 = \frac{d}{2}\left(h + \frac{d}{6}\right)$	$T_{17°\text{C.}}$
1·62 mm.	8·69 mm.	7·27 sq. mm.	484 dynes/cm.
2·09	6·65	7·31	486
		Mean value	485 dynes/cm.

A further determination of the surface tension of mercury was made by radiographing the rise of mercury between two flat vertical copper plates inclined at a

---

[*] *See* Anderson and Barr, Journ. Scient. Instr., I, 1, p. 9, October (1923).

[†] Cf. Bashforth and Adams, Capillary Action, p. 8.

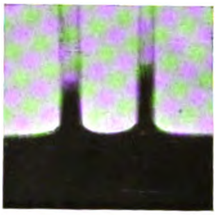


FIG. 1.

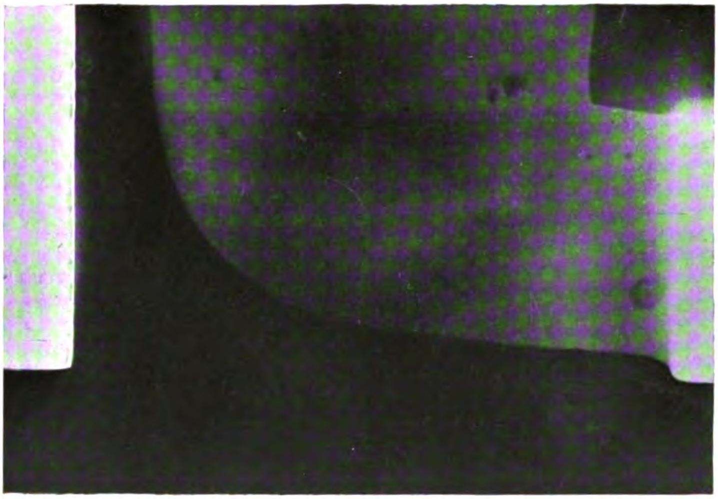


FIG. 2.

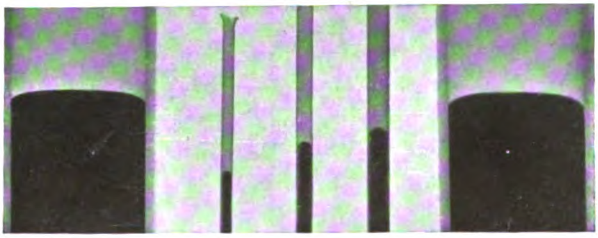


FIG. 3.

To face page 204]

UNIV. OF MICH.

small angle to one another. The radiograph shown in Fig. 2 was obtained with plates inclined at an angle of 0·0284 radian. The mercury surface appears as a rectangular hyperbola whose equation is $xy=251$ sq. mm. This gives the value

$$a^2 \equiv \frac{2T}{\rho g} = 0{\cdot}0284 \times 251 = 7{\cdot}13 \text{ sq. mm.}$$

and

$$T_{17^\circ\text{C.}} = 474 \text{ dynes per cm.}$$

The mean value of the surface tension of mercury at 17°C. given by these methods is 480 dynes per cm. It is in tolerable agreement with the value of 465 dynes per cm. at 20°C. obtained by Harkins and Grafton* but is considerably lower than the value of 547 dynes per cm. at 17·5°C. given by Quincke.†

Fig. 3 shows a radiograph of the depression of mercury in three steel tubes. The tubes were fixed in a horizontal tube connecting two glass reservoirs of diameter 18 mm. The level of the mercury in the reservoirs served as a surface of reference. The results of the measurement of the radiograph are given in Table II, a correction of 0·06 mm. having been made for the capillary depression in the reservoirs.

TABLE II.

Diameter of tube (d).	Capillary depression (h).	$a^2b = \frac{d}{2}\left(h + \frac{d}{6}\right)$
1·21 mm.	10·56 mm.	6·51 sq. mm.
1·83	6·63	6·34
2·52	4·80	6·58
	Mean value	6·48 sq. mm.

From the mean value of a^2b (=6·48 sq. mm.) and the value of a^2 (=7·21 sq. mm.) obtained in the first two experiments, the value of b, that is $\cos(\pi-\omega)$, where ω is the angle of contact, works out to be 0·899, so that the angle of contact between mercury and steel is 154° approximately.

The above examples serve to indicate the possibilities of the method. It can be employed for the solution of problems to which the usual methods of measuring surface tension are inapplicable and it has an advantage over these methods in that a permanent record is obtained which can be examined at leisure.

The authors do not intend to pursue the subject further. They have directed attention to the method in the hope that it will be of interest to those engaged in the study of capillarity.

In conclusion, they wish to take this opportunity of thanking Mr. T. A. Chalmers for his help in taking the radiographs.

DISCUSSION.

Dr. D. OWEN asked if the authors had tried radium as a substitute for X-rays, and if so with what results. In regard to the determination of the surface tension of mercury by ascent of a copper tube, it appeared that the results by this method agree with those obtained by more usual methods; so that the degree of contamination of the mercury by copper did not appear to affect the value appreciably. The value of the angle of contact using a steel tube comes out rather large: it would be of interest to have particulars of the method of cleansing the tube.

---

* Journ. Amer. Chem. Soc., 42, 2534 (1920).

† Pogg. Ann., 105, 35 (1858).

Mr. J. E. CALTHROP: I should like to ask Dr. Owen if the value of *h* for a tube showing capillary rise was measured from the " bottom " of the meniscus, because it is not evident from the photograph that such a measurement is possible. Also, in calculating the capillary rise or fall was any allowance made for the fact that the photographic plate was further from the X-ray source than the column casting the shadow? What was the approximate distance of the plate from the centre of a capillary tube?

Dr. V. E. PULLIN (communicated): The following application of radiography, somewhat similar to the work described by Dr. Owen and Mr. Dufton, was recently investigated in my laboratory, and will probably be of interest to the Society.

A manufacturing firm applied for information as to the possibility of reading the height of a mercury column in a steel tube used as a piezometer, the walls of the tube being 4 mm. thick and the bore 8 mm., and the tube was contained in a water-jacket.

It was found possible to obtain a sharp outline of the mercury surface in such a tube distant 45 inches from the focus of the X-ray tube, with an exposure of 10 seconds, using 5 milliamperes at 150 kilovolts.

By attaching to the steel tube, in the plane containing the axis of the tube, a lead screen having fine holes drilled through it at intervals of 1 mm., it was possible to obtain in a radiograph a record of the mercury level and a scale for reading its height.

Dr. OWEN said that the rays from radium had not been tried. He was of opinion that with such penetrating radiation the definition of the shadow would not be satisfactory for the purpose of measurement. As to the method of cleaning the steel tube, the inner surface was first polished by passing string covered with fine emery powder to and fro through the tube. The emery was removed by passing another length of string steeped in distilled water through the tube. Distilled water was afterwards passed through the tube, which was finally washed and dried with alcohol solution.

In reply to Mr. Calthrop, the value of " *h* " was obtained from the curved surface of the meniscus—the " bottom " of the meniscus in the tubes showing capillary rise, and the " top " of the meniscus in the tubes showing capillary depression. The definition of the meniscus in Fig. 1 had suffered in the reproduction, but the original could be measured to the required degree of accuracy. In calculating the values of surface tension allowance had in each case been made for magnification. This was determined either from the external dimensions of the tube and its shadow, or from the distances of the photographic plate from the object and the source. The distance between the plate and the centre of the capillary tube varied in the different experiments. In the experiment shown in Fig. 1 it was 10 mm. approximately.

XXIV.—THE EFFECTS OF TORSION UPON THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF ALUMINIUM, WITH SPECIAL REFERENCE TO SINGLE CRYSTALS.

By J. E. Calthrop, *M.A.*, *M.Sc.*, East London College.

Abstract.

An attempt has been made to find the changes produced by torsion in the conductivities of single aluminium crystals, and of the annealed and hard aluminium wires from which the crystals are prepared. The hard wire gave a decrease of a few parts in a thousand in the thermal conductivity, but no change greater than one part in 1,000 has been found in crystal wires. The decreases in the electrical conductivities, of the order of a few parts in 10,000, appear to be almost the same for all specimens.

I. Introduction.

The effects of strain upon the conductivities of metals are interesting from the point of view of the Wiedemann-Franz law, by which the ratio of the conductivities should remain constant at constant temperature. Bridgman* has investigated very thoroughly the effects of pressure and tension upon a large number of metals, and has found that the above law is not obeyed. For example, for tension upon aluminium, the metal in which we are at present interested, the changes in the specific conductivities, taken as unity, are :—

Thermal conductivity, $-3{\cdot}8\times10^{-6}$ per kg./cm.^{2},
Electrical conductivity, $-1{\cdot}3\times10^{-6}$ per kg./cm.^{2},

which values are corrected for changes in dimensions. The changes due to hydrostatic pressure are about five times greater than these.

The changes produced by torsion have been investigated by Smith,† and by Prof. Lees and the present author,‡ who agree in finding small decreases in both conductivities, the thermal changes being greater than the electrical. Smith took the changes to be proportional to the twist, and Calthrop as proportional to the square of the twist.

In the present Paper are described the results of tests, which have been made upon a hard wire, an annealed wire, and upon single crystals, prepared from similar hard wires. For the preparation of the crystals I am very much indebted to the kindness of Prof. H. C. H. Carpenter and Miss C. F. Elam, of the Royal School of Mines.

II. Preparation of the Specimens.

The composition of the aluminium used was : Al, 99·6 per cent. ; Fe, 0·2 per cent. ; Si, 0·2 per cent. Other impurities were negligible.

The annealed wire was prepared by being kept for three minutes at 400°C., and then being allowed to cool gradually during five hours, according to instructions to be found in a book, " Aluminium and its Alloys," by C. Grard.

---

* P. W. Bridgman, Proc. N.A.S., Vol. 59, No. 6 (1923).

† Smith, Phys. Rev., 28, pp. 107-121 (1909).

‡ C. H. Lees and J. E. Calthrop, Proc. Phys. Soc., Vol. 35, p. 225 (1923) ; Vol. 36, p. 168 (1924).

Miss Elam has personally prepared the single crystals by methods which have been fully described.*

After a preliminary heat treatment to remove hardness and to render the crystals equi-axed, a metal wire about 12 in. long is strained by tension to produce a 2 per cent. extension on a length of 3 in. The wire is then kept at a temperature of 550°C. for six hours, and the crystals finally etched with a 10 per cent. solution of caustic soda. They are so soft that great care is required to prevent strain, especially in the process of winding on the platinum coils used in the thermal measurements.

III. METHOD FOR THERMAL CONDUCTIVITY.

It is not proposed to describe the method in detail, as this has been done in the earlier Papers. The essence of the method is as follows :—

The wire to be tested is held in water-cooled clamps, which form the ends of a water-cooled, cylindrical chamber. Heat is supplied to the centre of the wire by means of a current in a manganin coil, and the temperatures at two points on one side of the heater are measured by two insulated platinum thermometers, wound round the test wire. A Callendar-Griffiths Bridge is used for measuring each resistance separately, the difference in the resistances, or the resistance of a coil which gives the variation of the temperature of the case.

The accuracy usually attained is that of one part in 1,000, but as the maximum length of the single crystals is only about 10 cms., it was thought well to reduce the lengths of the platinum thermometers, so that the accuracy for the single crystals is 0·15 per cent.

IV. THEORY OF THE METHOD.

It has been shown that :—

$$H=(qK\ .\ \cosh ax_0+hs\ .\ \sinh ax_D)\frac{v_B-v_A}{\sinh ax_B-\sinh ax_A}\cdot\frac{ab}{\sinh ab}$$

where H=Total supply of heat to half the wire.
q=Area of section of the wire.
K=Thermal conductivity.
h=Emissivity of the wire.
$a^2=\frac{ph}{qK}$, where p is the perimeter of the wire.
x_0=The distance of the near end of the heating coil from the clamp.
$x_D=x_0+\frac{1}{3}(x_C-x_0)$, where x_C=distance of the centre of heating coil from clamp.
v_B, v_A=Temperature excesses at distances x_B and x_A from the clamp.
s=Half the area of the wire covered by the heating coil.
$2b$=Length of wire covered by each of the platinum thermometers.

If S is the resistance of half the heating wire and the current is A amperes,

$$H=\frac{SA^2}{4{\cdot}18} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

---

* Carpenter and Elam, Proc. Roy. Soc., A., pp. 329-353 (1921); J. of Iron and Steel Inst., No. 1, 107, p. 175 (1923).

also v_B and v_A may be expressed in terms of the platinum resistances at the temperature of the case, R_0, r_0, and those during heating, R_1, r_1. Thus :—

$$v_B - v_A = \frac{35}{34} \cdot \frac{1}{\gamma}\left(\frac{R_1}{R_0} - \frac{r_1}{r_0}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

γ is the temperature coefficient of resistance for platinum, calculated from the resistance at the mean case temperature 15°C., and a reduction of 1 cm. from the 35 cms., the usual length of the platinum thermometer, is made for the portion soldered to the copper leads.

Finally, from (1), (2) and (3)—

$$\left(qK + hsx_D \frac{\sinh ax_D}{ax_D} \cdot \frac{1}{\cosh ax_0}\right) \frac{a \cosh ax_0}{\sinh ax_B - \sinh ax_A} \cdot \frac{ab}{\sinh ab} = \frac{\gamma SA^2}{4{\cdot}34\left(\frac{R_1}{R_0} - \frac{r_1}{r_0}\right)} \quad (4)$$

h has been taken as 0·0003 . $\frac{ab}{\sinh ab}$ may be taken as unity. The constant 4·34 becomes slightly greater for a coil smaller than 35 cms. K may easily be calculated from (4).

V. METHOD OF OBSERVATION.

In measuring the thermal conductivity, time was given for the heating current to become steady, when the resistance of the case-coil, the resistance of the hot thermometer, and the difference in the resistances of the hot and cold thermometers were read in this order. The heating current was then measured to one part in 10,000, by comparing the fall of potential it produced in a fixed length of manganin wire with that of a standard cell, and then it was switched off. After about ten minutes, the resistances were read in the reverse order.

Readings for no twist and for two twists were usually taken one day, and again for no twist after the wire had been left untwisted all night.

VI. METHOD FOR ELECTRICAL CONDUCTIVITY.

In order to avoid any possible differences in temperature coefficients, the resistances of two wires of the same kind were compared by the ordinary potentiometer method. The fall of potential down the wire to be twisted was balanced against the coils and slide wire of the same Callendar-Griffiths Bridge, placed in another circuit. The sensitivity was such that a change in the resistance of one part in 10,000 was equivalent to 0·3 mm. on the galvanometer scale. The mean of a

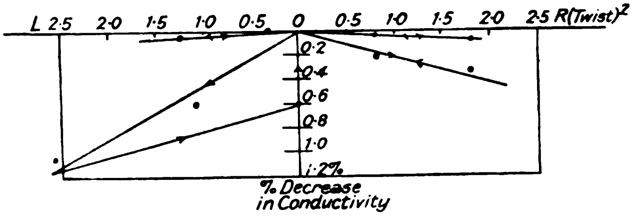


FIG. 1.—HARD ALUMINIUM.

The upper curve shows the decreases in the electrical conductivity, and the lower curve those in the thermal conductivity of a hard aluminium wire, plotted against the square of the twist which is measured in degrees per cm.

large number of readings both with direct and reversed current was taken, and the usual accuracy attained was one in 10,000, in a resistance of about 0·001 ohm, which was not found absolutely. A twisted hard wire was compared with a hard wire, a crystal with a crystal, and so on.

In the following tables, typical results are shown, with values of the twist in degrees per cm., and of the square of the twist. The resistance of the case coil is shown for each reading. 1°C. is equivalent to 0·0070 ohm.

VII. TABLES OF RESULTS.

(1) Hard aluminium wire. Diameter = 2·00 mm.
Current = 0·330 amp.; $x_C = 5·6$ cms.; $x_B = 4·7$ cms.; $x_A = 1·8$ cms.
Value of K from equation (4) = 0·495.
Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	$(\text{Twist})^2$.	Conductivity.	Per cent. Change.
20/4/25	2·5002	0	0	1·0000	...
	2·5019	0·89R	0·79	0·9978	−0·22
	2·5016	1·34R	1·79	0·9964	−0·36
22/4/25	2·5092	0	0	1·0000	...
12/5/25	2·5302	0	0	1·0000	...
	2·5297	1·07L	1·14	0·9940	−0·60
	2·5285	1·60L	2·56	0·9895	−1·05
14/5/25	2·5312	0	0	0·9940	−0·60
15/5/25	2·5330	0	0	1·0000	...
		Electrical	*Conductivity.*		
1/10/25	...	0	0	1·0000	...
	...	0·89R	0·79	0·9998	−0·02
	...	1·34R	1·79	0·9991	−0·09
	...	0	0	1·0000	...
	...	0·54L	0·29	1·0000	−0·00
	...	1·10L	1·21	·9994	−0·06
	...	0	0	1·0000	...

(2) Single crystal. Diameter = 1·92 mm.
Heating current = 0·330 amp.; $x_C = 4·8$ cms.; $x_B = 4·05$ cms.; $x_A = 1·05$ cms.
$K = 0·496$.
Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	$(\text{Twist})^2$.	Conductivity.	Per cent. Change.
17/2/25	2·5589	0	0	1·0000	...
	2·5581	1·04R	1·08	1·0000	...
	2·5607	0	0	0·9985	−0·15
19/2/25	2·5572	0	0	1·0000	...
	2·5563	1·04L	1·08	1·0015	+0·15
	2·5579	0	0	0·9985	−0·15
		Electrical	*Conductivity.*		
3/11/25	...	0	0	1·0000	...
	...	0·58R	0·34	0·9998	−0·02
	...	0·87R	0·76	0·9995	−0·05
5/11/25	...	0	0	1·0000	...
	...	0·58L	0·34	0·9998	−0·02
	...	0·87L	0·76	0·9993(5)	−0·06(5)
	...	0	0	1·0000	...

(3) Annealed wire. Diameter = 2·00 mm.
Heating = current 0·330 amp. ; x = 5·9 cms. ; x_B = 5·0 cms. ; x_A = 2·0 cms.
K = 0·490.
Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist)^2.	Conductivity.	Per cent. Change.
4/6/25	2·5537	0	0	1·0000	...
	2·5548	0·85R	0·72	1·0010	+0·10
	2·5560	1·29R	1·66	1·0005	+0·05
	2·5541	0	0	1·0005	+0·05
		Electrical	*Conductivity.*		
10/11/25	...	0	0	1·0000	...
	...	0·57R	0·33	0·9998	—0·02
	...	0·90R	0·81	0·9994	—0·06
	...	0	0	1·0000	...
	...	0·57L	0·33	0·9998	—0·02
	...	0·90L	0·81	0·9994	—0·06
	...	0	0	1·0000	...

(4) Few crystals. Diameter = 1·95 mm.
Heating = current 0·330 amp. ; x_C = 5·6 cms. ; x_B = 4·7 cms. ; x_A = 2·0 cms.
K = 0·490.
Thermal Conductivity.

Date.	Case Coil (ohms).	Twist ° per cm.	(Twist)^2.	Conductivity.	Per cent. Change.
18/6/25	2·5343	0	0	1·0000	...
	2·5337	0·90R	0·81	0·9990	–0·1
	2·5337	0	0	0·9995	–0·05
		Electrical	*Conductivity.*		
19/11/25	...	0	0	1·0000	...
	...	0·61R	0·37	0·9998	—0·02
	...	0·97R	0·94	0·9995	—0·05
	...	0	0	1·0000	...
	...	0·61L	0·37	0·9998	—0·02
	...	0·97L	0·94	0·9994	—0·04
	...	0	0	1·0000	...

These results are exhibited graphically in Figures 1 and 2.

VIII. Discussion of the Results.

In the tables given above it is to be remembered that the accuracy for the single crystal is 0·15 per cent., while for the hard, the unannealed and the wire consisting of a few crystals the accuracy in the thermal measurements is 0·1 per cent. These and similar results appear to show no change in a crystal wire greater than 0·1 per cent. in the thermal conductivity, though the hard wire gave decreases greater than this, in very reasonable agreement with the earlier results for an aluminium wire. On the other hand, the decreases in the electrical conductivities of the order of a few parts in 10,000 appear to be very much the same for the aluminium in all forms. The harder wire suffers a slightly smaller change than the softer forms, as Fig. 2

will show. Values for right and left twists have been plotted for the hard wire, while the values for the other wires are for right twists only, in order to save confusion.

Another point of interest is that there do not appear to be very large differences between the conductivities of the various wires.

Our values for the thermal conductivities were :—

Crystal A	0·496 C.G.S. units.
Crystal B	0·501 ,,
Hard Wire	0·495 ,,
Annealed Wire	0·490 ,,
Few Crystals	0·495 ,,

Agreement is more exactly tested for the electrical conductivites, which, however, were not measured absolutely. The ratio of the resistance of a hard wire to that of a crystal from the comparison of both with the same crystal, and with correction for dimensions, was 1·0030.

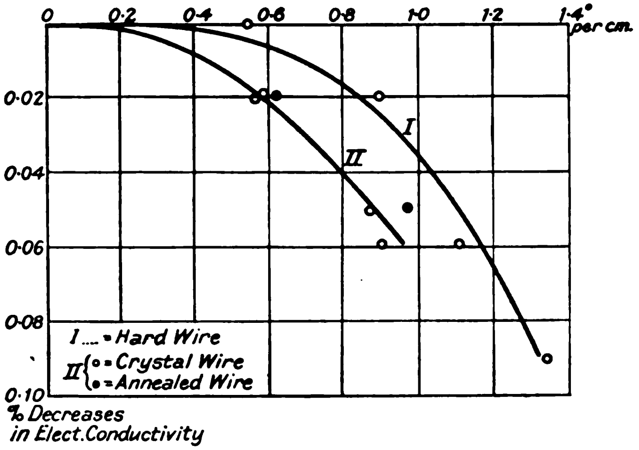


FIG. 2.—DECREASES IN ELECTRICAL CONDUCTIVITY.

The upper curve shows the decreases in the electrical conductivity of a hard aluminium wire, plotted against the twist, which is measured in degrees per cm. The lower curve shows the decreases for crystal and annealed wires. The black dots are for a wire consisting of a few crystals.

The above changes do not appear to be explained by the change in dimensions, as a change of 1 part in 40,000 for the twists used could not be detected. This was the limit of accuracy obtainable. Poynting's* results for steel and copper would lead us to expect a longitudinal extension and a lateral contraction of the order of 1 in 1,000,000.

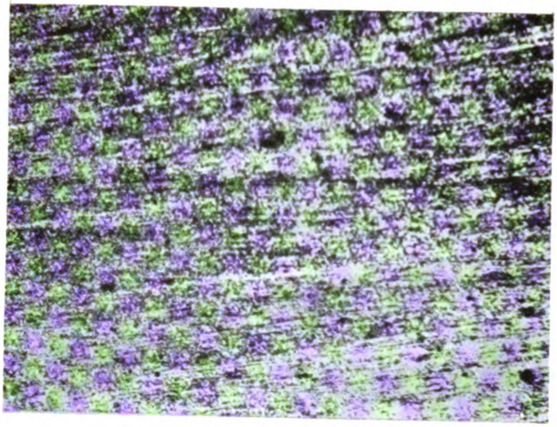
It would appear that in the process of drawing the crystals may become elongated or thread-like. Work by X-ray methods shows that the [111] direction of the crystal lattice lies parallel to the direction of drawing.

Eltisch and Polyani† found, in addition to the [111] direction, a smaller number

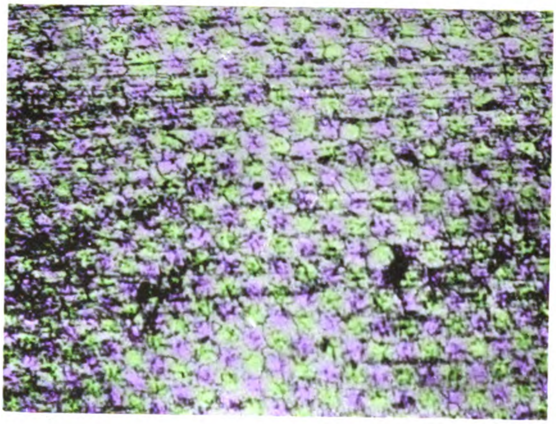
---

* Collected papers, p. 397.

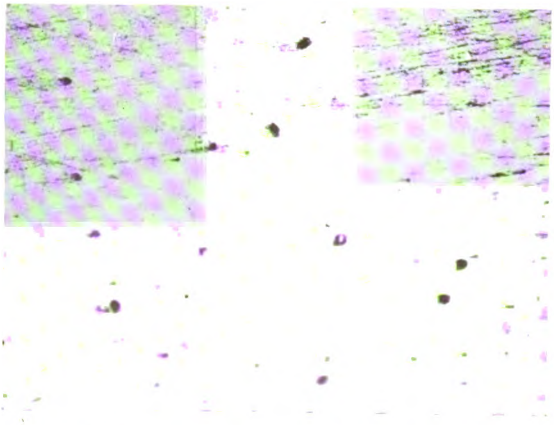
† Zeits f. Phys., 7, pp. 181-184 (1921); Zeits f. Phys. Chem., 99, pp., 332-337 (1921).



Aluminium Wire as Drawn ×100.



Aluminium Wire Annealed ×100.



Portion of Single Aluminium Crystal ×100.

[To face page 213

of crystals with [100] parallel to this direction, which effect was not very prominent in the later work of Sachs and Schiebold.*

I suggest that the larger changes in the thermal conductivity of the hard wire are because of this structure.

If the crystals are to follow the shear of the wire, they must be extended while undergoing lateral pressure. The density of the hard wire was 0·2 per cent. greater than that of a crystal wire, so that the changes found appear to be consistent with Bridgman's results, mentioned earlier in the Paper.

Annealing renders the crystals of more uniform size in all directions, as may be seen from the second photograph, and in this state the crystals would more easily follow the shear of the wire.

It is presumed that the changes in a crystal are small because the body is very isotropic. It is possible that some such lattice theory as J. J. Thomson's† might predict such changes from the distortion of the space-lattice, but Bridgman's‡ results for pressure on some non-cubic metal crystals lead him to believe that resistance is determined by the details of the atomic structure, and not merely by the distance apart of the atoms. Some idea of the differences in structure of the various specimens may be gathered from the micro-photographs, for which I am indebted to the kindness of a former pupil, Mr. E. Musgrave.

In conclusion, I should like to tender my sincere thanks to Prof. H. C. H. Carpenter and Miss C. F. Elam for providing the materials for this work, and to Prof. C. H. Lees, in whose laboratory the experiments have been made.

DISCUSSION.

Prof. O. W. RICHARDSON complimented the author on a very careful piece of work. He thought it remarkable that the thermal conductivity effect should be absent in the case of single crystals.

Miss C. F. ELAM said that it had given great pleasure to Prof. Carpenter and herself to furnish the author with single crystals, as they found it impossible to investigate all the properties of these themselves and were much interested in the results obtained by others. In finding the electrical conductivity of drawn metal less than that of single crystals the author was in agreement with previous results, but his relative values for the densities appeared to be inconsistent with the usual experience, which is that the drawn metal is less dense than the annealed. She did not think that the differences in conductivity between the various forms of the metal are mainly attributable to changes in the orientation of the crystals, for other physical properties are much affected when the metal is very slightly worked, while definite changes in orientation do not affect the physical properties to a corresponding extent.

Dr. E. H. RAYNER said that he noticed that the aluminium used contained 0·2 per cent. each of silicon and iron, both of which have a marked effect on electrical conductivity. It seemed doubtful whether such a small proportion of impurity can have a serious effect on the structure of a single crystal, yet it has been found that the addition of 0·4 per cent. of Si will alter the resistance of aluminium by 2 or 4 per cent. It has also been found that if the aluminium be treated with an alkali metal the Si loses its effect.

Mr. ROLLO APPLEYARD asked how far different specimens of the same kind differed from one another in density.

The Author, in reply, said that he did not insist on his suggestion that the effect of stress on conductivity is to be explained by distortion of the space lattice, but it might be anticipated that any changes due to such a cause would be small, since Bridgman has found that the resistances measured along different axes of non-cubic crystals differ by only 30 per cent. All the specimens examined were taken from the same stock of original material.

---

* Naturwissenschaften, p. 964, Nov. (1925).

† Phil. Mag., 44, p. 657 (1922).

‡ Proc. N.A.S., 10, pp. 411-415 (1924).

XXV.—A STUDY OF THE CONCURRENT VARIATIONS IN THE THERMIONIC AND PHOTO-ELECTRIC EMISSION FROM PLATINUM AND TUNGSTEN WITH THE STATE OF THE SURFACES OF THESE METALS.

By T. H. Harrison, *B.Sc.*, King's College, London.

Abstract.

An attempt has been made to measure the thermionic and photo-electric work functions for the same specimens of tungsten and platinum. It is found that in all cases the results depend greatly on the previous heat treatment of the material. In the case of platinum the curves showing the dependence of photo-electric sensibility on the wavelength of the irradiation are of four different types, while as regards thermionic properties the specimens can take up either a " large-emission " or a " small-emission " state, according to their treatment. The photo-electric work function of platinum appears to be greater than the thermionic, but no definite results were obtained for tungsten. The photo-electric curves obtained for both metals did not end abruptly so as to indicate a maximum wavelength for emission, but extended asymptotically towards zero emission in the direction of increasing wavelength. These irregularities in behaviour are attributed by the author to the state of the surface of the specimens.

Introduction.

THE photo-electric and thermionic work functions of tungsten and of platinum are known to be of the same order of magnitude under certain circumstances, and it is desirable to determine whether they are really equal. No measurements of both quantities have been made for the same specimen of either metal, and the differences known to exist between the work functions for different specimens make it impossible, from the available data, to establish or disprove the identity of the two work functions. The work described in what follows is an attempt, made at the suggestion of Prof. O. W. Richardson, to measure both quantities for the same samples of the two metals above mentioned.

Experimental Method.

Two specimens of tungsten and two of platinum were used for the work. These were enclosed in tubes which, in the case of the tungsten specimens, took the form shown in Fig. 1. In the first tube the tungsten was in the form of a plane spiral filament 12 cm. long and 0·23 mm. in diameter, while in the second (shown in the figure) a cylindrical spiral filament was used, so as to intercept more radiation.

In the case of platinum, a strip 10 cm. long, 1·5 mm. wide and 0·02 mm. thick was stretched vertically along the axis of a copper cylinder also 10 cm. long, which served as the anode, and which had suitable holes made half way along its length to form an entrance and an exit for the ultra-violet radiation. Two specimens of this metal too, were used in the work.

The vacuum was obtained by means of a Gaede rotary mercury pump, backed by a Geryk pump, and the pressures were measured by a McLeod gauge. Between the McLeod gauge and the photo-electric thermionic tube were a coconut charcoal tube and a mercury vapour trap, both of which could be immersed in liquid air. Without the use of liquid air a pressure of 10^{-4} mm. of mercury was obtainable, and in the latter experiments of 2×10^{-5} mm. With the aid of liquid air pressures completely immeasurable could be obtained, although when the filaments or strips were heated the pressure would rise to about 10^{-5} mm. unless the metal had previously been well " glowed out."

For the photo-electric measurements, a quartz mercury vapour lamp was used, the radiation of which was passed through a Hilger monochromatic illuminator. The telescope tube (the slit and eyepiece being removed) was fitted over the end of one of the tubes above described, the ultra-violet radiation passing through the quartz window, and the image of the collimater slit being formed at a slit inside the photo-electric tube from which the radiation diverged on to the tungsten spiral, or, in the case of platinum at the central portion of the platinum strip itself. The relative values of the energy in the various wavelength regions were assumed to be the same as those found by Compton and Richardson for similar apparatus.*

For the thermionic measurements, the tungsten spiral or the platinum strip was heated by passing an electric current through it which was measured by an ammeter, the resistance being simultaneously measured with a Wheatstone bridge.

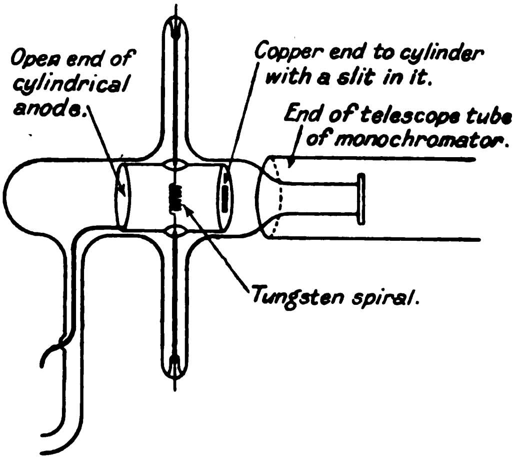

Open end of cylindrical anode.
Copper end to cylinder with a slit in it.
End of telescope tube of monochromator.
Tungsten spiral.

Fig. 1.—Diagram of the Second Tungsten Tube.

The photo-electric currents were measured with a quadrant electrometer with a sensitivity of 650 mm. per volt per metre scale distance.

The thermionic currents were measured for tungsten with a micro-ammeter with shunts and for platinum by a galvanometer with suitable shunts.

The photo-electric currents for different wavelengths in the mercury vapour lamp spectrum were measured and the photo-electric sensitivity curves were drawn. From these the long wave limit could be estimated.

For obtaining the thermionic work function, use was made of Prof. Richardson's formula $i=AT^{1/2}e^{-\varphi/kT}$, or $\log_{10} i-\frac{1}{2}\log_{10} T=\log_{10} A-(\varphi/2{\cdot}303k)T^{-1}$. Plotting the experimentally found values of $\log_{10} i-\frac{1}{2}\log_{10} T$ as a function of $1/T$, the curve should be, providing the nature of the surface does not change, a straight line, the inclination of which gives the work function φ.

---

* Compton and Richardson, Phil. Mag., 26, p. 549.

EXPERIMENTAL RESULTS FOR THE FIRST TUNGSTEN SPECIMEN.

(*a*) *Photo-Electric.*

For some time after the first tube had been baked and glowed, any photo-electric currents produced by light passing through the monochromator were too small to measure. After a further glowing of the tungsten filament, however, the sensitivity was increased, and a large number of sets of readings were taken over a considerable period, some at comparatively high pressures of 2 or 3×10^{-4} mm. of mercury without the use of liquid air, and others, with the use of liquid air, at pressures almost immeasurable on the McLeod gauge. Some of the later sets of readings were taken, after a further glowing of the filament, at a temperature of about 2,300°K. For several hours after this glowing the photo-electric currents did not re-appear, but after two or three days, the pressure never rising above 10^{-4} mm., readings almost identical with the previous ones were obtained. A typical set of readings is given in Table I below. It is to be noted that with an anode potential of 50 volts the photo-electric currents were no greater than with one of 2 or 3 volts.

TABLE I.—*Typical Set of Readings of Photo-Electric Current for the First Tungsten Tube.*

$p = 10^{-6}$ mm. Slit of monochromator 0·05 in. wide. Anode volts = 7.

λ in Å.U.	2,540	2,530	2,520	2,550	2,766	2,820	2,766	2,820	2,766	2,820	2,766	2,820
Deflection of electrometer in 5 mins. less dark current ...	15·2	16·3	13·5	17·1	2·0	1·6	2·0	1·8	2·0	1·9	2·2	1·7
λ in Å.U.	2,766	2,820	3,020	2,662	2,545	2,480	2,377	2,343	2,260	2,300	2,450	2,300
Deflection in 5 mins....	1·7	1·5	0·8	5·1	14·7	5·5	4·9	3·6	3·0	3·7	3·1	4·4

Dividing the photo-electric currents by the energy of the light beam at the corresponding wavelength, the sensitivity curve for tungsten is obtained. This is shown in Fig. 2. It must be borne in mind, however, that these photo-electric currents being extremely small, the accuracy cannot be great, and also that the relative energies in various parts of the spectrum of the mercury vapour lamp and monochromator combination used in these experiments may not be absolutely identical with those found by Compton and Richardson with similar apparatus. Nevertheless, for the purposes of this Paper, it will be sufficient to assume the identity of the two energy distributions.

The main point of interest in Fig. 2 is that the main part of the curve approaches the wavelength axis as if it would cut it at about 2,700 Å.U., but, instead of doing this, it bends round and finally approaches it so gradually as to make it appear asymptotic. This " asymptotic " extension of the photo-electric sensitivity curve appears in almost all the photo-electric experiments.

Later results on platinum show that only an insignificant part of this " foot " is due to stray light from the monochromator, hence it must be concluded that this " foot " is real, although its cause is obscure.

Neglecting the " foot," the long wave limit is at about 2,700 Å.U., otherwise it must be greater than 3,000 Å.U.

(*b*) *Thermionic.*

In the case of the tungsten specimens the temperature was estimated by two methods :—

(*a*) By the increase of resistance of the filament ;

(*b*) By the heating current, together with the known diameter of the filament.

The temperature required is that of the central portion of the filament, since the cooler ends emit relatively few electrons. Data regarding the allowance to be made for the cooler ends of the filament in estimating the temperature by the change in resistance of the filament, and also the relationship between the heating current the diameter of the filament and its temperature were obtained from a Paper by Stead.* The temperatures as estimated from the heating current are about 30° higher than those estimated from the change of resistance.

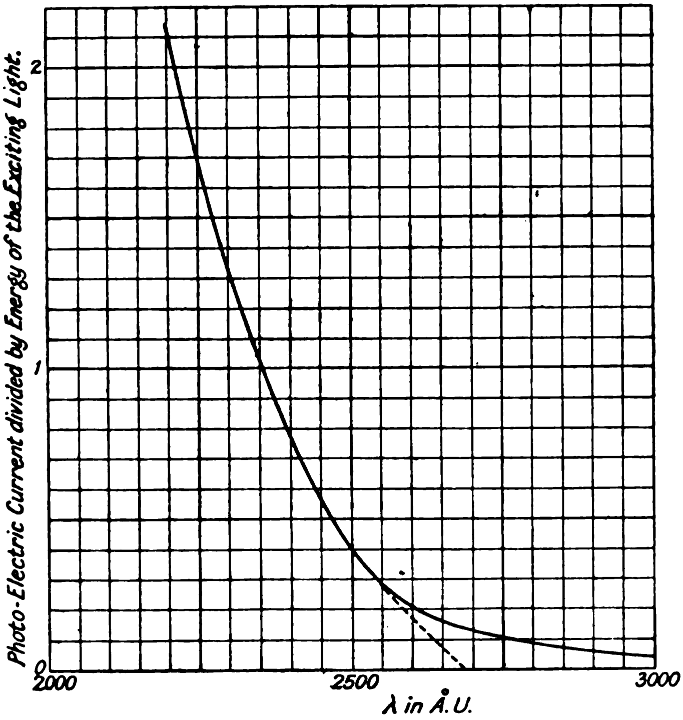


FIG. 2.—SENSITIVITY CURVE IN THE FIRST TUNGSTEN TUBE.

Notwithstanding a considerable amount of baking out of the tube and glowing the filament, a state was never reached in which no gas was evolved when the filament was first switched on ; nevertheless, after a short time the liquid air and charcoal would reduce the pressure to between 5×10^{-5} and 10^{-6} mm. Possibly better conditions might have been obtained eventually, but for the premature collapse of the tube in baking it out. Five sets of readings were taken, all at pressures between 10^{-5} and 10^{-6} mm., two sets with decreasing temperature and three with increasing temperature. The curves for $\log_{10}i - \frac{1}{2}\log_{10}T$ as a function of $1/T$, when T is estimated from the resistance, are shown in Fig. 3. With the exception of the readings in Set 3, the points are found to lie very close to straight lines, and the values of φ as calculated from the inclination of these straight lines are given below :—

---

* Stead, Journal of Inst. of Elec. Engrs., 58, p. 107 (1920).

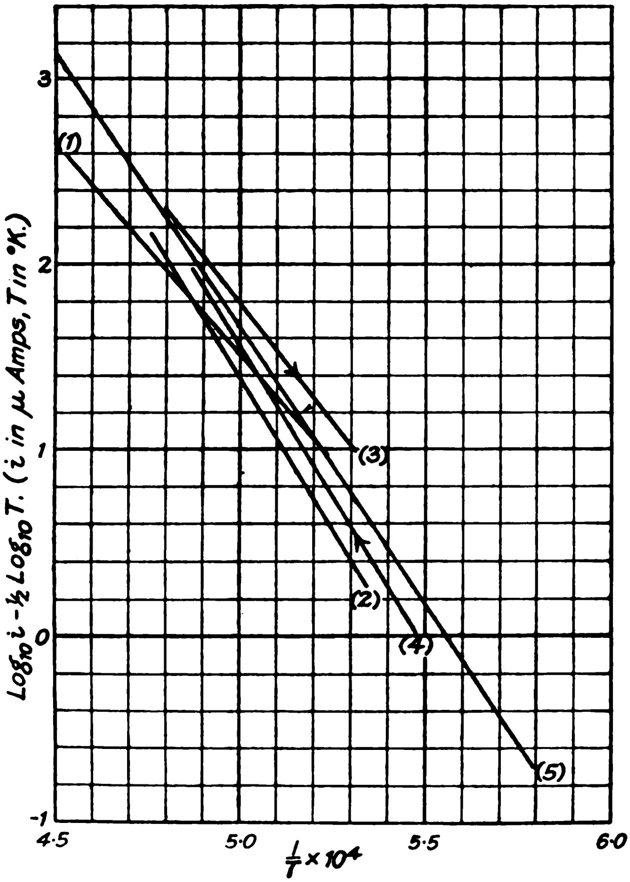


FIG. 3.—THERMIONIC CURVES OF TUNGSTEN.

Temperatures estimated from heating current	Set 1	Falling temperature.	$\varphi=4{\cdot}64$	volts	
	„ 2	Rising „	$\varphi=6{\cdot}32$	„	
	„ 3	Falling „	$\varphi=4{\cdot}8$	„	(about)
	„ 4	Rising „	$\varphi=5{\cdot}97$	„	
	„ 5	Rising „	$\varphi=6{\cdot}65$	„	
Temperatures estimated from change of resistance.	Set 1	Falling temperature.	$\varphi=4{\cdot}78$	volts.	
	„ 2	Rising „	$\varphi=6{\cdot}52$	„	
	„ 3	Falling „	$\varphi=5{\cdot}0$	„	(about)
	„ 4	Rising „	$\varphi=6{\cdot}57$	„	
	„ 5	Rising „	$\varphi=6{\cdot}00$	„	

As the temperature of the filament was increased, a certain amount of gas was evolved since the pressure would rise from about 10^{-6} mm. to about 5×10^{-5} mm. After a few minutes, however, the charcoal would absorb this gas, and the pressure again be almost immeasurably low, until the temperature of the filament was again increased. Thus, it appears likely that the difference between the work functions observed for rising temperature and for falling temperature is due to the presence of gas which apparently causes the work function to be higher while it is being evolved.

The value of the work function for falling temperatures is about 4·8 volts, and this agrees with that found by Davisson and Germer.* The long wave limit corresponding to 4·8 volts is 2,570 Å.U.

EXPERIMENTAL RESULTS FOR THE SECOND TUNGSTEN SPECIMEN.

As stated before, the second tungsten filament intercepted more light than the first. Further, the Gaede pump was improved and higher vacua obtained.

Before any measurements were made, the tube was baked out at 350°C. and the spiral heated to about 2,400°C. Upon attempting to make photo-electric measurements it was found that instead of having larger photo-electric currents than those previously obtained, as was expected, no measurable currents at all were produced by light passing through the monochromator. After 48 hours, however, the following extremely small photo-electric currents were measured.

TABLE II.

$p = 10^{-4}$ mm. Liquid air on trap, but not on charcoal.

	Anode volts = 7·5		Anode volts = 100.				
λ in Å.U.	2,540	2,540	2,540	2,480	2,450	2,378	2,26
Deflection of electrometer in 5 mins., less "dark current"	2·2	1·9	1·8	0·6	0·3	0	0·4

The "dark current" for the above set of readings gave a deflection of −0·8 cm. in 5 minutes when the anode potential was 100 volts, and +0·7 cm. when the anode potential was only 7·5 volts. These "dark currents" were measured several times with satisfactory agreement.

The tube was then rebaked several times to 350°C. for periods up to 15 hours, and the filament was again glowed, the pressure being reduced to 5×10^{-5} mm. without the use of charcoal. Then using liquid air on the charcoal, the pressure was reduced below the measuring capacity of the gauge. No photo-electric currents were measurable until after two or three days after the glowing of the filament. The set of readings given in Table III shows the exceedingly small currents which were then obtained.

TABLE III.

p not measurable. Anode volts = 7·5.

λ in Å.U.	2,540	2,380	2,260	2,054	1,975	1 943	1,850	Full light of lamp. No monochromator.				Glass screen.	Quartz screen
Deflection in 1 min.	0·4	1·2	1·1	0	0	0	0	21·4	23·8	23·6	30·0	−0·1	5
Deflection in 5 mins.	0·2	0·9	0·9	0	0	0	0	...	...	...	...	0	28·4

---

* Davisson and Germer, Phys. Rev., 20 (1922).

After another three days without heating the filament, the sensitivity increased to the values shown in Table IV.

TABLE IV.

$p = 10^{-6}$ mm. Anode volts = 7·5.

Nature of illumination.	2 cm. water screen.	Water screen.	Glass screen.	Full light.	Full light.	2 mm. quartz screen.	Quartz screen.	2 cm. methyl alcohol.	Methy alcohol screen.
Deflection in 1 min.	8·4	7·9	−0·1	170	170	40	40	11·4	12·5
Deflection in 5 mins.	25·9	25·9	0	...	...	...	...	34·4	...
Nature of illumination.	Glass screen.	Full light.	Å. 2,537	Å. 2,652	Å. 2,470	Å. 2,450	Å. 2,378	Glass screen.	... ...
Deflection in 1 min.	−0·3	180	0·7	0·6	−0·3	0	0·6	0·5	...
Deflection in 5 mins.	0·0	...	1·9	0·9	+0·1	0·3	1·2	0·5	...

Several further attempts were made at various pressures to obtain larger photo-electric currents but without success. In one of the sets of readings without the use of the monochromator, taken soon after a glowing of the filament, the 2 mm. thick fused quartz screen was found to cut down the photo-electric current to about one-thirtieth of its previous value. On lowering the liquid air flask for a fraction of a second from the trap, the photo-electric currents were increased to the values shown in Table IV, without any rise of pressure being recorded by the McLeod gauge, but on removing the liquid air from the charcoal tube, no further increase in photo-electric sensitivity took place, although the pressure gradually rose from below 10^{-6} mm. to 5×10^{-2} mm.

It is thus seen that the long wave limit for tungsten is distinctly variable. The effect of glowing the tungsten to about 2,400°K. is to increase the photo-electric work function. With lapse of time, however, the work function again becomes smaller, but this decrease in work function can be made to occur almost instantaneously by lowering the liquid air from the trap for a fraction of a second. When the tungsten has not been recently glowed, the long-wave limit is certainly higher than 2,650 Å.—i.e., its photo-electric work function is less than 4·6 volts. About two or three hours after glowing the tungsten the wavelength limit would appear to be in about the same region as that found by Hagenow*—namely, at about 2,300 Å., with a work function of about 5·36 volts. In all cases, the photo-electric sensitivity curves seem to tail off as the wavelength is increased, the photo-electric currents in the " tail " being too small to ascertain whether there is a definite end to it.

GENERAL CONCLUSIONS FOR TUNGSTEN.

Although photo-electric and thermionic measurements have been made upon the same sample of tungsten, it is found that very small changes in the previous history affect both work functions considerably. It follows that the tungsten was probably in a different state for the photo-electric measurements and for the thermionic measurements. Until the thermionic and photo-electric work functions can be measured whilst the metal is in the same state, there can be no proof of their identity, but, on the other hand, there is nothing in the above results which renders such an identity improbable.

---

* Hagenow, Phys. Rev., 13, p. 415 (1919).

EXPERIMENTAL RESULTS FOR THE FIRST PLATINUM SPECIMEN.

(*a*) *Photo-Electric.*

Owing to the disappointing nature of the results obtained with tungsten, it was decided to carry out similar measurements on platinum in the hope that more positive information might be obtained.

Two samples were used, as described in the first section of the Paper. A large number of photo-electric readings with the first strip were taken before any thermionic readings were taken at all. The sensitivity curves showing the photo-electric currents per unit energy of monochromatic light at various wavelengths could be divided into five types. These are not shown, owing to lack of space, but similar ones are shown in Fig. 4 for the second sample of platinum.

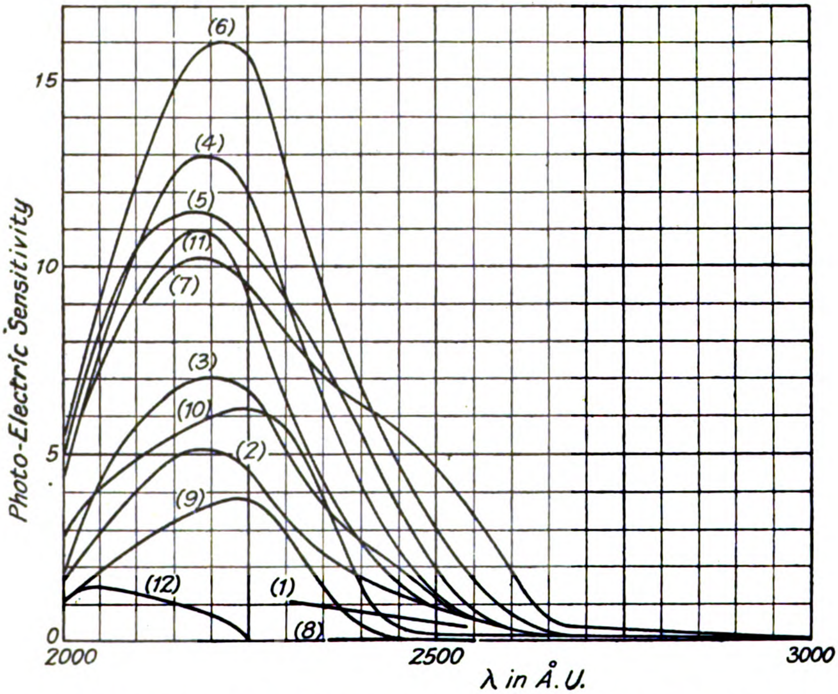


FIG. 4.—PHOTO-ELECTRIC SENSITIVITY CURVES FOR SECOND SAMPLE OF PLATINUM.

Type 1 occurred several hours after a glowing of the platinum to a reddish yellow heat, and also after a further glowing at a brighter yellow heat, the pressure during the photo-electric readings being below the least measurable value. The shape of the curve was similar to that of curve 2, Fig. 4, but the average sensitivity was only half as big, whilst the "foot" of the curve was longer, showing a long wave limit of 2,900 Å.

Type 2 was found an hour or two after glowing to a brighter yellow heat, and was almost identical with curve 2, Fig. 4, showing a long-wave limit of 2,660 Å.

Type 3, found two or three days after Type 2, without any intervening heat treatment, and with the pressure kept below the measurable limit for the whole time, had the same shape as Type 1, with an increase in sensitivity of about 50 per cent. for all wavelengths, the long wave limit being at 2,900 Å.

Type 4, found an hour or two after glowing the platinum for seven hours at about 1,425°C., with a pressure of 5×10^{-6} mm., was of the same shape as curve 4, Fig. 4, the sensitivity at all wavelengths being 0·8 times as large. The long-wave limit was at 2,660 Å.

Type 5, found 24 hours after Type 4, the low-pressure being maintained and no heat treatment being given in the meantime, showed a very large increase in the sensitivities for wavelengths between 2,500 Å. and 3,000 Å., besides a small increase for the shorter wavelengths. It corresponded to curve 7, Fig. 4, but extended very much further towards longer wavelengths, the long wave limit being 3,000 Å. At 2,800 Å. the sensitivity was 1·0 on the same scale as Fig. 4, whilst the maximum sensitivity at 2,250 Å. was 11·5. In all of these types there was a maximum sensitivity at about $\lambda=2,200$ Å.

The nature of these five typical sensitivity curves depended upon the previous heat treatment of the strip and the interval of time since that treatment.

In no case that was investigated with the first strip was there any evidence of a definite long wavelength limit, the currents dying down gradually with increasing wavelength until they became too small to detect. There was, however, in most of the curves a more or less defined region where the curve, instead of continuing to meet the wavelength axis, bent round and proceeded at a small inclination to it, as if the final approach might be asymptotic. Part of this " foot " was doubtless due to stray light of shorter wavelengths, scattered by the monochromator, and some attempt was made to discover to what extent this was the case by using as a filter a solution of cobalt and aluminium chlorides. The solution absorbed too much light, however, and the attempts were discontinued, since further sensitivity curves threw some light on the subject, and showed that at any rate a considerable fraction of the currents in the " foot " was due to the monochromatic light of wavelength indicated on the drum of the monochromator. When, for example the third and fourth types of sensitivity curves for the first platinum strip were compared, it was seen that at $\lambda=2,700$ Å.U. the apparent sensitivity for Type 3 was about four times that for Type 4, and yet the stray light of short wavelengths in Type 4 must have been twice as effective as that for Type 3, the condition of the monochromator being the same in both cases. Thus, in Type 3 it is justifiable to say that at 2,700 Å.U. at least seven-eighths of the ordinate is due to radiation of $\lambda=2,700$ Å.U., but that the remaining one-eighth may be due to stray radiation. It thus appears that the greater part of the " foot " of the sensitivity curves is real, and not due to stray light. On the other hand, it is not justifiable to say that the wavelength axis is asymptotic to the curve, since there are no means of measuring the exceedingly small photoelectric currents for the longer wavelengths, and since the spurious " stray light " currents may become relatively larger as the wavelength increases.

In the absence of any definite " long-wave limit " the sensitivity curves have been prolonged to meet the axis by dotted lines from the points at which the " foot " begins, and the wavelength at the intersection of these dotted lines and the axis will be refered to as the " long-wave limit."

Comparing the five typical curves found for the first strip, in all of which the anode was maintained at 7·5 volts, or more than sufficient to promote saturation, it is found that the immediate effect of heating the strip is to increase the sensitivity of the platinum for the shorter wavelengths, and decrease it for the longer wavelengths, but, with lapse of time, the after effect of this heat treatment is an all-round increase in sensitivity, notwithstanding the fact that the pressure has by the use of charcoal and liquid air been kept too low to be measured by the McLeod gauge. The effect of heating the platinum to white heat 1,425°C., is of the same kind as that of heating it only to yellow heat, but is more pronounced. Before the 1,425°C. glowing the " long wave-limit " is at 2,900 Å.U., while an hour afterwards the limit is at 2,660 Å.U. After 24 hours, however, the pressure being very low the whole time, λ_0 is at 3,000 Å.U., and the sensitivity is very high.*

(*b*) *Thermionic.*

The temperatures of the strip were measured by its resistance, this being measured in arbitrary units corresponding to the addition of 1 ohm in the variable part of a Post Office box. The " end-effects " were allowed for in the temperature estimations, a subsidiary experiment being carried out with two thermionic tubes, each with a strip of platinum of the same breadth and thickness, but of different lengths.

Having applied the corrections for the effects of the leads and end cooling found by this subsidiary experiment, the temperatures of the strip can be calculated from the known resistivity-temperature curve of platinum.

Six sets of thermionic readings were taken, and the graphs of $\log_{10} i - \frac{1}{2} \log_{10} T$ were plotted as a function of $1/T$. These graphs were similar to those shown in Figs. 5 and 6, i being measured in units of about 10^{-9} amps. by a galvanometer, and T being measured in °K. It was noticed that, until the platinum had been heated for a long time at a pressure as low as possible with liquid air and charcoal, the thermionic currents were large, but after a time they quickly decreased to about one-thousandth part of their previous value. For this reason, it is convenient to call the state in which the larger thermionic currents are obtained " The Large Emission State " and the other " The Small Emission State."

The values of work functions are given in Table V :—

TABLE V.

	Large Emission State.			Small Emission State.		
	Set 1.	Set 2.	Set 3.	Set 4.	Set 5.	Set 6.
Pressure	10^{-4}	10^{-6}	10^{-4}	10^{-6}	5×10^{-6}	5×10^{-6}
φ in volts	3·77	4·33	3·97	4·09	3·52	4·23
Corresponding λ_0 ...	3,275	2,850	3,110	3,010	3,500	2,920

---

* It is worthy of note that at the commencement of the glowing at 1,425°C., which preceded the measurements shown in Curve 4, the thermionic current density was about one-quarter of that for tungsten at the same temperature—i.e., 30 micro-amperes for the whole strip—but after two hours it fell to about one-thousandth of this value, the pressure never being more than 5×10^{-5} mm., and during the latter part of the glowing not more than 10^{-5} mm. In taking the measurements which contribute to the fourth type it was noticed that there was a growth of sensitivity at the longer wavelengths with time, so that all the time the sensitivity curve was gradually approaching that of the fifth type.

At the highest temperature above those used in taking the readings of Set 1, the thermionic currents decreased quickly approaching the "small emission" state.

In Set 2 it is probable that the temperature estimations are too high owing to evaporation of the strip at temperatures approaching its melting point during the course of the previous set of readings of Set 4, and that in consequence the value of the work function is over estimated.

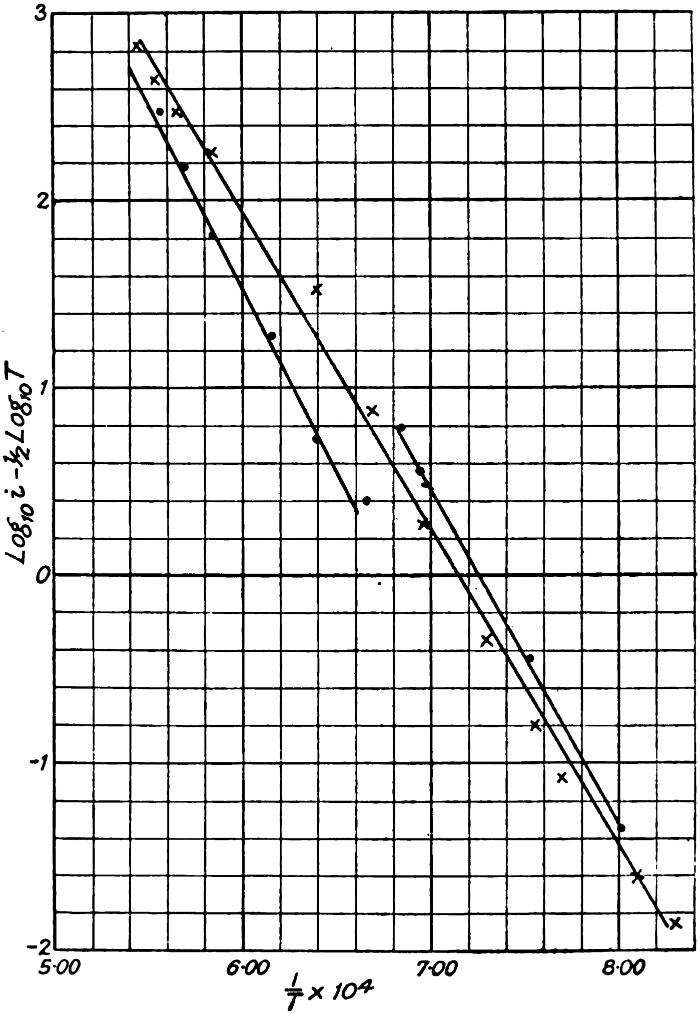


FIG. 5.—THERMIONIC CURVES FOR SECOND SAMPLE OF PLATINUM (Large Emission State).

In subsequent measurements this effect of the strip becoming thinner owing to evaporation of the platinum at high temperatures was allowed for in the following way: Knowing the temperatures in the earlier measurements as estimated from the resistance, and the heating currents corresponding to these temperatures, a curve connecting heating current and temperature was drawn, so that in the later readings the temperatures could be estimated from the heating current as well as from the resistance. That estimated from the heating current is too low, while that estimated from the resistance is twice that amount too high. The deviations of the estimations from the true temperature were about 50°, showing the extent of the thinning of the strip through evaporation.

In some cases, measurements were made for both rising and falling temperature. Usually the curves found for rising temperature are rather steeper than those for falling temperature, the heating possibly altering the work function somewhat.

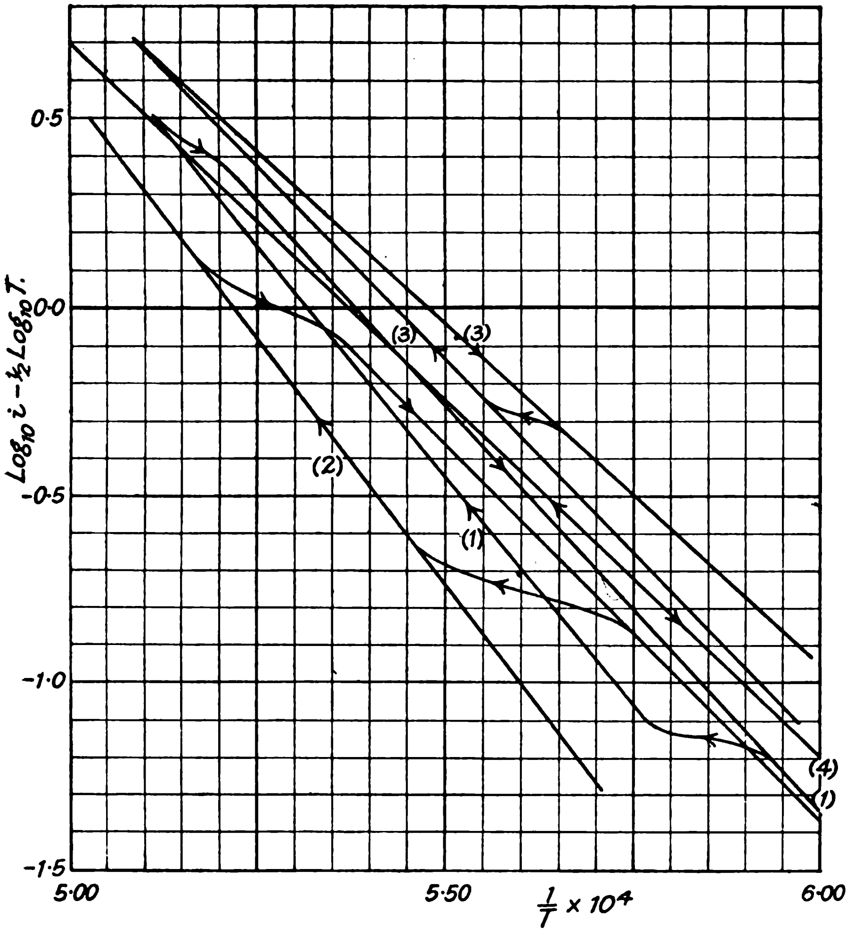


FIG. 6.—THERMIONIC CURVES FOR SECOND SAMPLE OF PLATINUM (Small Emission State).

EXPERIMENTAL RESULTS FOR THE SECOND PLATINUM SPECIMEN

After the sixth set of readings with the first platinum strip it fused. The second strip was then placed in the same tube with the same leads, its breadth and thickness being the same as those of the first strip, but its length being 10·5 cm. instead of 10 cm.

The photo-electric sensitivity curves of the second strip are shown in Fig. 4. Details of these curves are :—

Curve 1—$p=10^{-6}$ mm., found ½ hour after bright yellow hot glowing.

Curve 2—$p=10^{-6}$ mm., found 2½ hours afterwards.
$\lambda_0=2{,}650$ Å. $\varphi=4{\cdot}66$ volts.

Curve 3—$p=10^{-6}$ mm., found 4½ hours afterwards.
$\lambda_0=2{,}650$ Å. $\varphi=4{\cdot}66$ volts.

Curve 4—$p=10^{-6}$ mm., found about 1 hour after glowing to 1,600°C.
$\lambda_0=2{,}650$ Å. $\varphi=4{\cdot}66$ volts.

Curve 5—$p=10^{-6}$ mm., found about 3 hours afterwards.
$\lambda_0=2{,}650$ Å. $\varphi=4{\cdot}66$ volts.

Curve 6—p too low to measure, found a few hours after thermionic readings, during which a temperature of 1,700°C was reached.
$\lambda_0=2{,}650$ Å. $\varphi=4{\cdot}66$ volts.

Curve 7—p immeasurably low, found a few days after the aforementioned glowing.
$\lambda_0=2{,}700$ Å. $\varphi=4{\cdot}57$ volts.

Curve 8—$p=2\times10^{-6}$ mm., found 2 or 3 minutes after a half-hour's glowing at 1,650°C.

Curve 9—$p=2\times10^{-6}$ mm., found a few minutes after Curve 8.
$\lambda_0=2{,}450$ Å. $\varphi=5{\cdot}04$ volts.

Curve 10—$p=2\times10^{-6}$ mm., found about 1 hour after Curve 9.
$\lambda_0=2{,}480$ Å. $\varphi=4{\cdot}98$ volts.

Curve 11—$p=10^{-6}$ mm., found 16 hours after Curve 10.
$\lambda_0=2{,}600$ Å. $\varphi=4{\cdot}8$ volts.

Curve 12—Found 3½ minutes after glowings at 1,700°C.
p immeasurably low. $\lambda_0=2{,}250$ Å. $\varphi=5{\cdot}48$ volts.

These curves are mostly of the same form as those for the previous strip, but no readings were taken after a dull yellow hot glowing and before the more severe heat treatment. Except for Curve 12, there is no evidence that there is a definite " long wave limit," and again it is noticed that stray light is not wholly responsible for the " foot " of the curves. The estimations of the long wave limit is as before, made by continuing the curves, by dotted lines from the point where the " foot " begins to cut the wavelength axis.

The thermionic curves of the second strip are shown in Figs. 5 and 6, those in Fig. 5 relating to the " large emission " state, and in Fig. 6 to the " small emission" state, these states being found for the second strip as well as for the first.

In Fig 5, Set 1 (points marked •) is in two parts, half an hour intervening between them. In both cases $p=10^{-4}$ mm., and the anode voltage=200.

For the lower temperature part $\varphi=3{\cdot}61$ volts, the corresponding $\lambda_0=3{,}420$ Å.

For the higher temperature part $\varphi=4{\cdot}07$ volts and $\lambda_0=3{,}030$ Å.

Set 2 (points marked X)—$p=10^{-4}$ mm. Anode volts=200.
$\varphi=3{\cdot}42$ volts. $\lambda_0=3{,}600$ Å.

In Fig. 6—

Curve 1, with rising temperature—$p=2\times10^{-6}$ mm. Anode volts=200.
$\varphi=4{\cdot}88$ volts. $\lambda_0=2{,}530$ Å.
With falling temperature $\varphi=4{\cdot}27$. $\lambda_0=2{,}890$ Å.

Curve 2, with rising temperature—$p=2\times10^{-6}$ mm.
$\varphi=5{\cdot}17$ volts. $\lambda_0=2{,}390$ Å.
Falling temperature—$p=2\times10^{-6}$ mm.
$\varphi=3{\cdot}97$. $\lambda_0=3{,}110$ Å.

Curve 3—$p=2\times10^{-6}$ mm.
Rising temperature $\varphi=4{\cdot}08$ volts. $\lambda_0=3{,}020$ Å.
Falling temperature $\varphi=3{\cdot}62$ volts. $\lambda_0=3{,}410$ Å.

Curve 4—For both rising and falling temperature.
$\varphi=3{\cdot}76$ volts. $\lambda_0=3{,}280$ Å.

After the fifth photo-electric curve was taken, the first thermionic measurements, as shown in Curve 1, Fig. 5, were made. Following this, but under better vacuum conditions, Curve 1, Fig. 6, was taken, and after that Curve 2, Fig. 5, followed by Curve 2, Fig. 6.

After the severe heat treatment of the platinum during the course of these thermionic measurements, photo-electric Curve 6, Fig. 4, was found, from which it is seen that although this heat treatment has considerably increased the photo-electric sensitivity it has affected the " long-wave limit " very little. Notwithstanding the very high sensitivities at the shorter wavelengths, the " foot " of the curve lies very close to the axis showing that " stray light " currents at the longer wavelengths are quite small. The photo-electric Curve 7 was found a few days after Curve 6, the after-effect of the heat treatment being to increase the " long-wave limit," but to decrease the sensitivities at shorter wavelengths.

Hitherto no photo-electric measurements have been made until about an hour after the platinum has been heated. It is seen, however, that changes do occur with time after the heat treatment, so, in order to find the immediate effect of a white hot glowing of the platinum, it was heated to 1,670°C. in the course of a half-hour's glowing, and as soon as possible after switching off the heating current, photo-electric measurements were made. These are shown in Curve 8, Fig. 4, and it is noticed that for radiation of wavelength of 2,360 Å.U. and above, there are no measurable photo-electric currents. It would therefore, appear that the large decrease in thermionic currents from the " large " to the " small emission " state in the course of prolonged heating to high temperature under the best vacuum conditions is accompanied by a large decrease in the photo-electric sensitivity. In the course of a few minutes, however, the sensitivity increases as witnessed by Curve 9, which was found a few minutes after Curve 8. This increase in photo-electric sensitivity and " long-wave limit " takes place under the very best vacuum conditions obtainable. At the same time the thermionic " small emission " state changes to the " large emission " state, but providing the vacuum is good only a very small amount of heat treatment is necessary to cause a reversion to the " small emission " state. About an hour after Curve 9, the measurements for Curve 10 were made, which shows an increase in sensitivity and in the " long-wave limit." Sixteen hours later, Curve 11 was found, showing a large increase in sensitivity with a correspondingly large increase in the "long-wave limit." The thermionic readings for Curve 3, Fig. 6, were then made. The difference between the work functions for rising and falling temperatures is even more marked than in the case of the first strip, and it seems that, even with the best vacuum that could be obtained, the heating does alter the surface. After the first strip had fused, for example, the remnants of it were found to be pitted, and it is, therefore, not surprising that the work function should change somewhat. The strip was now heated nearly up to its melting point, and on switching off the heating current, the electrometer was connected up. The full light of the mercury vapour lamp gave an unmeasurably high photo-electric current with the electrometer, while a filter of 1½ cm. of distilled water cut this current down so that it gave a deflection of 30 cm. in 5 seconds. Twelve hours later the sensitivity curve was almost identical with Curve 11. After another heating to about 1,700°C. more photo-electric measurements were made. For about 3 minutes after the heating current is switched off, there is a large but gradual decreasing non-photo-electric current, for which the previous large thermionic current is held to be responsible. This spurious current may be due to leakage from the glass walls of electrons which have been deposited there thermionically. In any case it certainly is not photo-electric, and it prevents photo-electric measurements, from being made until about 2½ minutes after the heating current is switched off.

Photo-electric measurements after the above-mentioned heating to 1,700°C. showed at first no measurable current for $\lambda=2,360$ Å., but after ten minutes it had reappeared.

In order to obviate the difficulties due to an increasing sensitivity with time, a new type of set of photo-electric measurements was then made. The strip was heated for 10 minutes to about 1,650°C. before each photo-electric measurement, and then the deflections of the electrometer were measured every quarter of a minute, except during the first 3 minutes after the heating current had been switched off. Similar results were obtained to those mentioned above. The thermionic measurements for Curve 4, Fig. 6, were then made, after which the photo-electric readings shown in Table VII, in Curve 12, Fig. 4 and in Fig. 7. Before each photo-electric measurement the strip was glowed to about 1,700°C. for 5 minutes.

TABLE VI.

p almost unmeasurable. Slit 5/100 in. wide. Anode volts = 7·5.

λ in Å.U.		1,850	2,040	2,140	2,240	2,360	2,540
Electrometer readings at a time after switching off heating current of—	3 mins.	0	0	0	0	0	0
	4 mins.	0·8	1·8	2·3	0·2	0	0·5
	5 mins.	1·8	3·3	3·5	2·9	0·7	0·9
	6 mins.	2·7	5·0	7·2	6·2	1·9	1·5
	7 mins.	4·1	6·6	10·8	10·1	3·2	1·6
	8 mins.	5·4	8·4	14·3	14·9	5·9	2·2
	9 mins.	6·7	10·6	18·9	20·2	8·6	2·2
	10 mins.	7·5	12·5	23·0	27·5	12·6	2·4

From the curves in Fig. 7, the rate of growth of the photo-electric currents which growth takes place even in the best vacuum that could be obtained, can be deduced. After three minutes, the rate of growth is a maximum for λ = about 2,200 Å.U. It is possible that if photo-electric measurements could be made immediately after the platinum had cooled, no photo-electric currents would have been found to exist. Assuming, however, that the rate of growth of photo-electric currents for, say, 5 minutes after the heating current had been switched off, is linear, it would appear from the above results that photo-electric currents are produced by light of wavelength 2,040 Å.U. and 2,140 Å.U., but not for $\lambda=2{,}240$ Å.U. and above this.

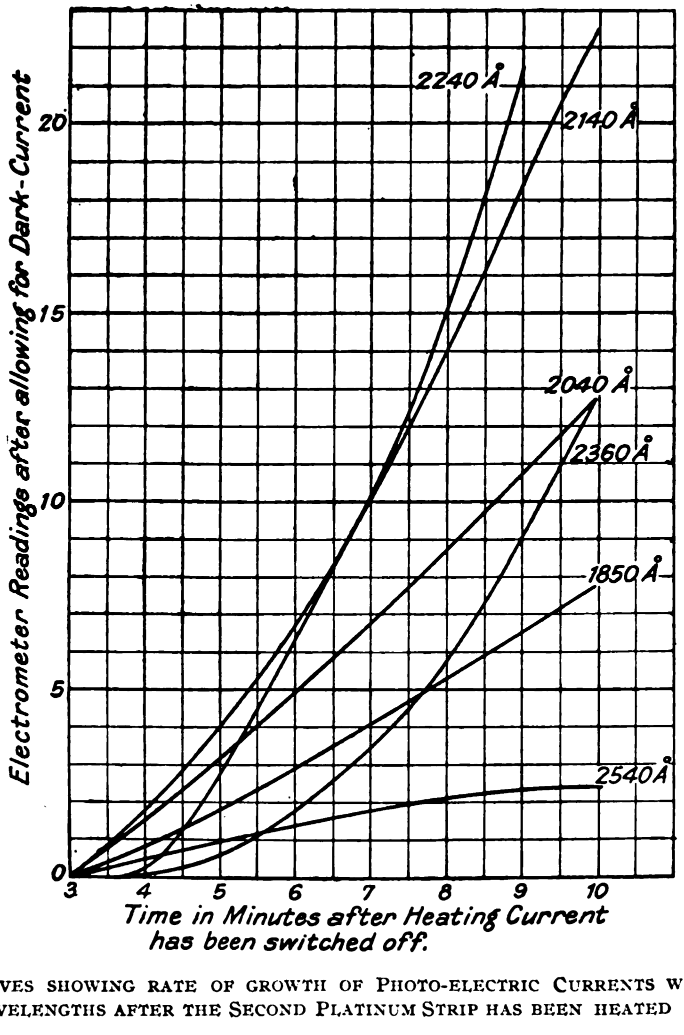


Fig. 7.—Curves showing rate of growth of Photo-electric Currents with time for given Wavelengths after the Second Platinum Strip has been heated to 1,700°C.

The sensitivity curve for 3½ minutes after switching off the heating current is shown in Curve 12, Fig. 4, a noteworthy result being that there is no " foot " to the curve, but within the sensitivity of the apparatus there is a definite point where the photo-electric currents cease to be produced.

Another point is that in this curve there is no apparent maximum sensitivity within the range of wavelengths investigated.

GENERAL CONCLUSIONS FOR PLATINUM.

The photo-electric curves for platinum may be classified into four types.

(1) Those found after a yellow hot glowing.

(2) Those found within an hour or so of a white hot glowing.

(3) Those found several hours after a white hot glowing.

(4) Those found 3 minutes after a long glowing to a temperature approaching the melting point under the best vacuum conditions.

The thermionic curves can be classified into two groups.

(1) Those corresponding to the " large-emission " state.

(2) Those corresponding to the " small-emission " state.

Any intermediate states seem to be unstable, for the change over from the one state to the other only occupied a few minutes from the large to the " small emission " state, whilst from the small to the " large emission " state, the change was instantaneous if the pressure were suddenly but slightly increased by lowering the liquid air from the trap for a fraction of a second. If the platinum were hot and in the " small emission " state and the heating current were switched off, on gradually reheating the strip it was found that the new thermionic currents for relatively low heating currents were larger than they would have been if the platinum had remained in the " small emission " state, but that on heating the platinum to a higher temperature, a very rapid reversion to the " small emission " state would occur. It thus seems very likely that the " large emission " state thermionic results correspond to the second class of photo-electric sensitivity curves, while the thermionic " small emission " state corresponds to the fourth class of photo-electric curves. It was impossible to find thermionic curves to correspond to the photo-electric states 1 and 3, since the glowing always changes these to states 2 and 4.

Identifying the photo-electric states 2 and 4 with the " large " and " small emission " states the results may be classified as shown in Table VII.

TABLE VII.—*Photo-Electric and Thermionic Work Functions of Platinum.*

First Strip.								Second Strip.							
Large emission state.				Small emission state.				Large emission state.				Small emission state.			
Thermionic.		Photo-electric.		Thermionic.		Photo-electric.		Thermionic.		Photo-electric.		Thermionic.		Photo-electric.	
ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0	ϕ	λ_0
3·77	3,275	4·65	2,650	4·09	3,010	...	...	3·61	3,420	4·65	2,650	4·88	2,530	5·48	2,250
*4·33	2,850	...	...	3·52	3,500	...	...	4·07	3,030	...	...	4·27	2,890	...	...
3·97	3,110	...	...	4·23	2,900	...	...	3·42	3,600	...	...	5·17	2,390	...	...
...	...	...	...	...	...	...	...	...	...	...	...	3·97	3,110	...	...
...	...	...	...	...	...	...	...	...	...	...	...	4·08	3,020	...	...
...	...	...	...	...	...	...	...	...	...	...	...	3·62	3,410	...	...
...	...	...	...	...	...	...	...	...	...	...	...	3·76	3,280	...	...

---

* This value is believed to be too high on account of the thinning of the strip, which was not accounted for.

On the whole it seems that the thermionic work function for platinum in the " small emission " state is if anything slightly higher than for the " large emission " state, whilst the photo-electric work function is much higher for the former state.

In all cases the photo-electric work function is higher than the thermionic, but the difference is much more marked for the " small emission " state. For the " small emission " state, the photo-electric work function is measured three minutes after thermionic measurements have been made under the best vacuum conditions, and the photo-electric work function is undoubtedly for this state over 30 per cent. greater than the thermionic.

Whatever may be the cause of the variations in the work functions, there can be no doubt about the fact that heat treatment increases the photo-electric work function more than the thermionic. It reduces the thermionic currents to about one-thousandth of their previous value, and also the photo-electric sensitivity considerably, but while the thermionic work function is but slightly increased, if at all, the photo-electric work function is considerably increased. Another effect of the heat treatment is to decrease greatly the photo-electric sensitivities in the " foot " of the curves, so that eventually this " foot " ceases to exist (within the sensitivity of the apparatus), and the curve is more nearly in accordance with the theoretical curve of Professor Richardson based on the principles of statistical equilibrium*.

The results in the photo-electric curves are very similar to those obtained by Sende and Simon,† Suhrmann,‡ and Tucker,§ but differ from those of Welo.‖ Apparently, however, Welo did not heat his platinum foil to a sufficiently high temperature for a sufficiently long time to obtain the condition which is termed above the " small emission " state. One difference between the above results and those of Sende and Simon, Suhrmann and Tucker is that in the above results the effect of a white hot glowing is not only to increase the sensitivity, but also to decrease temporarily the " long-wave " limit.

It should be noted that Sende and Simon, and Tucker both find that immediately after platinum is cooled after an intense heating, the light from a mercury vapour lamp produces only about one-thousandth of the previous photo-electric current, and that they come to the conclusion thereby that the true long-wave limit of platinum is very little, if any, greater than 1,850 Å.U.

Whilst the above results do not show such a marked decrease in the long wave limit, yet they do suggest that under some conditions it might be reduced to less than 2,250 Å. Tungsten also shows the same property of producing relatively large photo-electric currents under some conditions which disappear after a strong heating.

It might be suggested that the strong heating of platinum merely reduces the photo-electric currents without altering the long wave limit. This is not so, for it is seen that the strong heating reduces the sensitivities at longer wavelengths to zero, whilst at shorter wavelengths the reduction is only slight.

---

* Richardson, Phil. Mag., 23, p. 615, and 26, p. 549.

† Sende and Simon, Ann. der Physik, 65. p. 697 (1921).

‡ Suhrmann, Ann. der Physik, 67, p. 43 (1922).

§ Tucker, Phys. Rev., December (1923).

‖ Welo, Phil. Mag., 45, p. 593 (1923).

GENERAL CONCLUSIONS.

In conclusion, it must be said that the above results show that the photo-electric work function of platinum is greater than the thermionic, very definitely so when the platinum for both measurements is in the state referred to above as the " small emission " state. For tungsten, no definite results were obtainable in respect of this question ; and if the tungsten is in the same state for both thermionic and photo-electric measurements, the results here show no reason for supposing the two work functions to be different. Nevertheless tungsten and platinum are alike in their behaviour in so far as strong heating of either of them increases its photo-electric work function. The greater part of the " foot " of the photo-electric sensitivity curves appears to be due to the state of the surface of the metal, perhaps to gas, since under the better vacuum conditions it dwindled away and finally vanished.

In conclusion, I should like to take this opportunity of thanking Professor Richardson for suggesting these experiments and for his helpful advice during their course.

DISCUSSION.

Prof. O. W. RICHARDSON said that the Paper sets more problems than it solves. The rate of growth of photo-electric activity with time and various other points need further investigation. The author's original aim was to settle the identity of the thermionic and photo-electric work functions, but he had been baffled by the effects of obscure changes in the surfaces of the specimens. Previous work had been done by Young and the speaker with potassium, but this metal was unsatisfactory to work with, and it had been expected that more definite results would be obtained with less easily contaminated metal surfaces. The surprising results actually obtained opened up considerable possibilities of further research.

Prof. A. O. RANKINE pointed out that the two work functions were more likely to be identifiable if they were measured under the same experimental conditions as to temperature. Would it not be preferable to be content with a much smaller thermionic current and to measure it with the electrometer, so as to equalise the temperature conditions ? The view that threshold potentials are very definite quantities did not seem to be borne out in the present instance.

Dr. J. H. VINCENT said that in the photo-electric experiments the asymptotic " foot " of the curve showing the dependence of photo-electric current on wavelength was presumably restricted by the difficulty of getting sufficiently intense low-frequency radiation directed upon the filament inside the enveloping anode. Would it not be possible to insert an additional filament into the tube and to use this as a source of radiation ? The results would be rough on account of the mixed character of this radiation, but the conditions would be substantially black-body conditions and some idea of the wavelengths involved could thus be obtained. Had not the substance of the present results been obtained by Prof. Richardson in his original investigations made twenty-five years ago ?

Dr. LEWIS SIMONS said the author seemed to have succeeded in controlling the changes in photo-electric sensibility very easily; but, personally, he had found great difficulty, when dealing with very slow electrons, in controlling the nature of the metal surfaces satisfactorily. The extreme variability of the emissivity of metal surfaces perhaps had a bearing on the work of De Broglie and Whiddington on the verification of the quantum theory for irradiation by X-rays, where the nature of the surfaces has not been particularly studied. Would the author say how far it had been possible to keep the pressure constant in experiments lasting a considerable time, in view of the fact that the results had been found so extremely sensitive to slight changes of pressure ? In conclusion, he would suggest that since the photo-electric current is carried by electrons moving with mixed velocities, its interpretation is very doubtful : the energy of this current would be a far more significant quantity.

Dr. E. H. RAYNER said he would like to make an addition to Prof. Rankine's suggestion. Would it not be possible to reduce a given photo-electric current to, say, half its value, and then restore the original strength by a change of temperature ? In this way thermionic and photo-electric measurements could be made under conditions as nearly as possible identical.

Mr. W. V. Mayneord (communicated): It is desired to bring to the notice of the author a Paper by Woodruff (Phys. Rev., Vol. 26, p. 655, November, 1925) on the Photo-electric Emission from Platinum.

Effects similar to those obtained by Mr. Harrison are described, fresh specimens dipped in nitric acid being photo-electrically inactive, but restored by heating to 250°C. by an electric current through them, though heating in an oven to a higher temperature did not restore sensitiveness. An interesting point arising from the results due to Woodruff is that the specimen rendered insensitive by heating to a very high temperature (say 1,300° K) was yet sensitive to the radiation from a tungsten filament within the tube, showing that the insensitiveness appears to be due to a shift of the threshold to wavelengths less than those transmitted by quartz. Again, a specimen heated to 1,300°K for 17 hours showed no emission under the action of a mercury lamp for two months though air was often admitted and pumped out again. Restoration is effected by moderate heating, as above. Many other phenomena and relevent details are discussed by Woodruff, whose results are in many respects similar to those described in this Paper.

Author's reply (communicated): I am glad to have had brought to my notice the Paper by Woodruff, whose results when compared with mine are very interesting. The same variability in both work functions is found in both cases, and so far as the effect of heat treatment is concerned there appears to be perfect accord between Woodruff's results and mine. Woodruff's samples of platinum, however, are more electro-negative than mine both thermionically and photo-electrically; his photo-electric currents are much smaller than those I obtained, for whilst in many cases he obtained no photo-electric current even with the full light of a quartz mercury-vapour lamp or iron arc, there was always a fairly large photo-current in similar circumstances in my experiments. Similarly, in Woodruff's results, the thermionic work function φ is given in three cases as 5·34, 6·12 and 9·22 volts respectively, whereas in mine in no case was there a value of φ exceeding 5·17 volts, the average value being about 4·0 volts. Further, my thermionic measurements were made over a more extended range of temperature.

It is difficult to see why two samples of platinum obtained from different sources should not be equally electro-positive, for the only difference in treatment between the two cases is that Woodruff's samples were treated with nitric acid whereas mine were not. The behaviour of Woodruff's platinum is very similar to that of my first tungsten sample, both photo-electrically and thermionically.

With regard to Professor Rankine's, Dr. Vincent's and Dr. Rayner's suggestions, it now appears that Woodruff attempted to measure both the work functions for the same temperature, and that he employed an additional tungsten filament inside his photo-electric tube. It is obvious that, at any rate for tungsten, photo-electric measurements need to be made using radiation of wavelengths shorter than those transmitted by quartz, and possibly more use could be made of some internal source of ultra-violet radiation, such as a tungsten filament.

With regard to Dr. Simon's remarks, in order to obtain the energy of the photo-electric current a knowledge is required of the distribution of energy and mean energy of the electrons for each wavelength used. I have no experimental data in this respect. By the use of liquid air, the pressure can be kept constant for at least two days, and very often for three days, at a value below the detecting limit of a McLeod gauge.

XXVI.—THE ANALOGY BETWEEN RIPPLES AND ACOUSTICAL WAVE PHENOMENA.

By A. H. Davis, *D.Sc.*, Physics Department, The National Physical Laboratory.

Abstract.

The extent of the analogy between cylindrical sound waves and waves on the surface of a liquid is studied. It is established for inviscid media that as regards velocity potential the differential equations are similar provided the disturbance is small and is harmonic in type. It is then shown that the velocity potential in a field of inviscid surface waves may be used to represent that in a field of cylindrical sound waves, provided the size of any obstacle bears the correct relation to the wavelength of the disturbance. In the case of a liquid having a depth greater than half the wavelength, it further follows that the height of a surface wave is a measure of the condensation of air in the corresponding acoustical condition.

The effect of moderate viscosity is of the same type for sound waves and for surface waves; it is most marked for short wavelengths, and it decreases amplitudes without appreciably altering the wavelength. The decrease in amplitude depends upon the viscosity, and upon the time which has elapsed since the commencement of free oscillations, or, for maintained oscillations, since the disturbance concerned left the source. For surface waves further damping occurs if the depth is less than half a wavelength, and the apparent viscosity may be appreciably increased by contamination of the surface by means of a film of oil of excessive thinness. Viscous effects are generally negligible in the case of sound, but they are appreciable for the water waves that would usually be used in a small ripple tank not greater than, say, 10 ft. in size. Mercury waves are much less affected by viscous damping than water waves.

Experiments conducted with model obstacles in a ripple tank showed that the effects of the meniscus around the obstacle and of the amplitude of the source were not important. When the water becomes stale on exposure—and presumably contaminated—the relative distribution of ripples around obstacles is appreciably modified, but not to an extent which would correspond to any very marked change in the loudness of a sound.

Experiments have also been conducted, outside the limits of strict mathematical analogy, using an impulsive disturbance instead of a maintained train of waves. When it is recognised that a sound pulse travels out singly, whereas with ripples subsidiary wavelets accompany the main pulse, the correspondence between ripple photographs and sound pulse photographs is most striking.

Illustrations are given of the use of a ripple tank in connexion with architectural acoustics, and of its general value where wave phenomena are concerned.

GENERAL wave phenomena are somewhat elusive to the imagination and water waves have frequently been used to illustrate them. Tyndall(1) made early use of ripples for this purpose in connexion with the propagation of light. Later Vincent(2) obtained his well-known photographs giving examples of reflection, refraction, diffraction and interference: he studied the analogue of an optical zone plate and of a simple diffraction grating, and his ripple measurements agreed well with the usual formulæ.

Ripples in a small tank appear, also, to be specially suitable for illustrating acoustical phenomena, for in these the wavelength is usually comparable with the size of any objects concerned. As early as 1844 we find Scott Russell,(5) in connexion with the acoustics of buildings, referring to the study of the behaviour of sound by using the water wave analogy, and pointing out that, in general, ripples are not completely analogous to sound waves. Watson(3) and Michel(4) have studied the acoustic features of buildings by such means, and a ripple tank has been in use for this purpose at the National Physical Laboratory for some time. The object of this Paper is to elucidate the conditions under which the analogy is valid and to illustrate its use.

I. MATHEMATICAL ANALOGY BETWEEN WATER WAVES AND SOUND WAVES.

Lagrange, Scott Russell(6) and Lamb(7) have referred to the close similarity between the equations for cylindrical waves of sound, and those for the propagation of certain waves on the surface of an inviscid liquid. The surface waves concerned are of the gravity type in which surface tension plays no appreciable part, and they are restricted to the case where, in comparison with the depth of the liquid, the height of the wave is small and the wavelength is great. As is the case with sound, the velocity of these waves is independent of the wavelength. The analogy is quite general and extends to the boundary conditions.

When surface tension is concerned there is no general analogy, for in these circumstances the velocity of a water wave depends upon its wavelength. Experiments could be carried out to emphasize this difference. On the other hand, these surface waves may be produced so conveniently with ordinary laboratory apparatus that we now proceed to study the extent to which, in spite of the differences, ripples may be used in strict analogy to sound waves. The equations will be limited in the first instance to propagation in inviscid fluids.

Sound Waves.

For sound waves the equation of continuity is

$$\nabla^2\varphi - ds/dt = 0 \qquad \dots\dots\dots\dots \quad (1)$$

where φ is the velocity potential at a point, and s the condensation as usually defined. Small quantities of the second order have been neglected.

We have also the dynamical relation

$$c^2 s = \partial\varphi/\partial t \qquad \dots\dots\dots\dots \quad (2)$$

where c is the velocity of sound waves.

Whence, eliminating s,(8)

$$\partial^2\varphi/\partial t^2 = c^2\nabla^2\varphi \qquad \dots\dots\dots\dots \quad (3)$$

For the case of cylindrical waves of which the axis is parallel to the axis of z, we have

$$\frac{\partial^2\varphi}{\partial t^2} = c^2\left(\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2}\right) \qquad \dots\dots\dots\dots \quad (4)$$

The general equation covering the propagation of cylindrical waves of sound of harmonic form $\partial^2\varphi/dt^2 = -\omega^2\varphi$ may thus be written,

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + k^2\varphi = 0 \qquad \dots\dots\dots\dots \quad (5)$$

where $k = \omega/c$. Clearly $k = 2\pi/(\text{wavelength})$.

At rigid boundaries we have(9) the condition

$$\partial\varphi/\partial n = 0 \qquad \dots\dots\dots\dots \quad (6)$$

Water Waves.

For waves on the surface of an incompressible liquid the equation of continuity is

$$\nabla^2\varphi = 0 \qquad \dots\dots\dots\dots \quad (7)$$

where φ is the velocity potential at any point in the liquid.

Taking the axis of z vertically downwards, the equation of continuity and the condition of zero vertical motion at the level bottom $z=l$ are both satisfied by$^{(10)}$

$$\varphi=\varphi_1\cosh k(z-l) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where

$$\frac{\partial^2\varphi_1}{\partial x^2}+\frac{\partial^2\varphi_1}{\partial y^2}+k^2\varphi_1=0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Obviously φ_1 represents a disturbance to which the disturbance at any depth z is proportional, the constant of proportionality falling off rapidly as the depth increases. It may be noted that this control condition is of the form desired for analogy to cylindrical sound waves. It remains to find the value of k.

In terms of φ the pressure condition for small motions$^{(11)}$ is

$$\delta p/\rho=gz-\partial\varphi/\partial t \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where ρ is the density of the fluid, and g the acceleration due to gravity.

If h denote the elevation of the surface at the point x, y, and T the constant surface tension, the pressure at the surface due to capillarity is $-T(\partial^2h/\partial x^2+\partial^2h/\partial y^2)$. Consequently, from (10) the pressure condition at the free surface is

$$\frac{T}{\rho}\left(\frac{\partial^2h}{\partial x^2}+\frac{\partial^2h}{\partial y^2}\right)=gh+\frac{\partial\varphi}{\partial t} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

except perhaps within a meniscus at a boundary, where the surface tension force cannot be regarded as vertical. Differentiating with respect to t and noting the kinematical surface condition,

$$\partial h/\partial t=-\partial\varphi/\partial z \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

the surface pressure equation takes the form$^{(11)}$

$$\frac{T}{\rho}\left(\frac{\partial^3\varphi}{\partial x^2\partial z}+\frac{\partial^3\varphi}{\partial y^2\partial z}\right)=g\frac{\partial\varphi}{\partial z}-\frac{\partial^2\varphi}{\partial t^2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Applying equation (8) to this, a relation for the surface is obtained which, for harmonic motion $\partial^2\varphi/\partial t^2=-\omega^2\varphi$ satisfies (9) provided k has the value given by

$$\omega^2/k^2=(Tk/\rho+g/k)\tanh kl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

Thus for small harmonic surface waves, the general equation for the disturbance at the surface of the liquid is

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+k^2\varphi=O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

It is readily shown$^{(11)}$ from (12) that the velocity c of propagation of harmonic surface waves is given by $c=\omega/k$. Obviously $k=2\pi/\lambda$, as was also the case with sound waves.

At rigid boundaries we have the condition

$$\partial\varphi/\partial n=O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

The Analogy.

We have thus seen that the differential equation

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+k^2\varphi=O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

is satisfied for harmonic disturbances both by cylindrical sound waves and by waves upon a water surface.

The general theory of functions of this type shows that the potential φ_P at any point P within a region to which the equation applies is determined by the values of φ and of $\partial\varphi/\partial n$ at the boundary. The formula is(12)

$$\varphi_P = -\frac{1}{4}\int D_0(kr)\frac{\partial\varphi}{\partial n}ds + \frac{1}{4}\int \varphi\frac{\partial}{\partial n}D_0(kr)ds \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

where the integrations are performed around the boundary and where $D_0(z) = (2/\pi)\int_0^\infty e^{-iz\cosh u}du$.

Now in considering equation (18), we may note that for a family of boundaries of similar shape but of different size the directions of the normals ∂n at corresponding points will be the same ; further, at rigid boundaries $\partial\varphi/\partial n$ has the value zero both for sound waves and for ripples. The values of kr at corresponding points within the different boundaries will be the same provided r varies as $1/k$—that is, provided r varies as λ ; or, in other words, if the linear dimensions of the model boundaries are proportional to the wavelength of the disturbance set up within them.

Consequently, if we have two similar regions in which this scale relation is satisfied, and to which equation (17) applies—say a region of sound waves and a region of ripples—and if we arrange the disturbance at the boundaries of the two regions to be such that values of φ and $\partial\varphi/\partial n$ correspond, then the disturbance φ_P at all corresponding points within the region will correspond exactly.

Having established this analogy in terms of velocity potential, we may show that within a certain limitation the height h of ripples may be taken as a measure of the condensation s of air at the corresponding point in a sound field. The complete analogy is between hk and s.

We have from 2

$$s = \frac{1}{c^2}\frac{\partial\varphi}{\partial t} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

As regards ripples, however, we see from (11) that in general h is not simply proportional to $\partial\varphi/\partial t$, owing to a term involving the curvature of the disturbed surface. However, from (12) and (8) we find $\partial h/\partial t = k\varphi_1 \sinh kl$. Consequently, for harmonic disturbance we have $\partial^2 h/\partial t^2 = k \sinh kl(\partial\varphi_1/\partial t) = -\omega^2 h$. Applying this result to a combination of (8) and (11), and using (14), we find that the curvature $(\partial^2 h/\partial x^2 + \partial^2 h/\partial y^2)$ is equal to $-k^2 h$.

It then follows that (11) may be written in the form

$$hk = \frac{1}{c^2}\frac{\partial\varphi}{\partial t} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

provided $\tanh kl = 1$, as is approximately the case when the depth of liquid exceeds half the wavelength.

On comparing (19) and (20) we see that for ripples of a given wavelength (since $k = 2\pi/\lambda$) the height of a ripple is a measure of the condensation of air at a corresponding point in the acoustic field.

Effect of Viscosity and Allied Phenomena.

The introduction of viscosity complicates the equations both for sound waves and surface waves.

Stokes⁽¹³⁾ first evaluated the effect of viscosity in the case of sound. For plane harmonic sound waves it is found that the amplitude of free waves dies away exponentially with time t, being proportional at any instant to⁽¹⁴⁾ $e^{-t/\tau}\cos(\omega t+\varepsilon)$, where $\tau=3/2\nu k^2$, and ν is the kinematical viscosity of the air. For the case where a constant disturbance $u=a\cos\omega t$ is maintained in the plane $x=0$, we find⁽¹⁵⁾ $u=ae^{-x/l}\cos\omega(t-x/c)$ where $l=c\tau$. The wave amplitude diminishes exponentially as it proceeds. It will be noted that, since $l=c\tau$, the decay in amplitude suffered in reaching a distance x from the source is that calculable from the time modulus τ and the time interval t involved. In both proofs $1/kc\tau$ is assumed small. For sound waves in air this condition is satisfied, and, if λ be expressed in centimetres, we find $l=9{\cdot}56\times\lambda^2\times10^3$. The effect of viscosity on amplitude is thus very slight except for sounds of very short wavelength.

Kirchhoff⁽¹⁶⁾ showed that a further .cause of dissipation of sound energy is to be found in the thermal pocesses consequent upon alternate rarefactions and condensations of air. A complete investigation taking into account this thermal effect as well as viscosity shows that the effect is equivalent to an increase in the kinematic viscosity ν, but the order of the effect is unchanged.

The effect of viscosity on harmonic surface waves is similar to that for sound. By a method which applies when the depth is greater than, say, half the wavelength, Lamb⁽¹⁷⁾ shows that the wave velocity is unaltered by viscosity, and that the time modulus of decay τ in this case is given by $\tau=1/2\nu k^2$, provided $1/kc\tau$ is small. The condition is usually satisfied for mobile liquids unless the wavelength is excessively small. Presumably, in fields of continuously maintained harmonic ripples, the total viscous attenuation attained in reaching a given point would be given by the factor $e^{-t/\tau}$, where t is the time which has elapsed since the ripple in question left the source. If this is so, relative intensity values along a wave front would not be affected in spite of the general attenuation experienced by the wave.

Expressing τ in terms of λ, and evaluating in the case of water, we find approximately $\tau=\lambda^2$ seconds.*

Table I gives details of waves on clean water of depth greater than half the wavelength.

TABLE I.—*Surface Waves on Water.*
(Depth greater than $\lambda/2$.)

Frequency. per sec.	Wavelength. cm.	Velocity. cm. per sec.	Number of oscillations in which amplitude falls to $1/e$ of its undamped value.
3·5	13	45·3	590
5·0	6·55	33·2	220
7·5	3·46	26·1	91
10·0	2·38	23·8	57
13·2	1·73	23·2	41
20	1·20	23·9	29
30	0·87	26·0	23
50	0·59	29·8	18
100	0·36	36·7	13

---

* The modulus τ is the time in which the ripples decay to $1/e$ of the amplitude they would have in the absence of viscosity.

The effect of viscosity is seen to be appreciable for water waves of short wavelength. The use of long waves would involve an unduly large ripple tank.

For mercury we find $\tau=10\lambda^2$, a value about ten times as great as the value for water, so that viscous effects are much reduced when mercury* is used. For general use mercury has, however, the disadvantage that the surface is not easy to clean, and the cost of large areas of sufficient depth is considerable. A clean water surface can be obtained very easily by simply refilling the cleaned tank with a fresh supply.

The effect of contamination of a wave surface depends upon the nature of the contamination. The general effect would be to alter the surface tension, and thus to affect the relation between wavelength and velocity. This in itself would not affect the validity of the analogy, provided the relation between the wavelength and the scale of the model were preserved. However, there is a special form of contamination, such as that in which an exceedingly thin oil film, say, not more than one or two millionths of a millimetre in thickness, covers the water thickness. The calming effect of such a film appears to be due to the increase of surface tension of the film which occurs when its thickness is reduced by stretching. Assuming that such a film of oil renders the wave surface practically inextensible, Lamb calculates the time modulus of decay(18) $\tau=(8/\omega\nu k^2)^{1/2}$. The ratio of this to the modulus obtained on the hypothesis of constant surface tension is assumed small; for water it is approximately equal to $(2/\lambda c)^{1/2}$. The calming effect of such excessively thin films would be very great; thicker films would not show the effect.

II. EXPERIMENTAL.

Various experimental arrangements have been used from time to time in the production and study of ripples. The late Lord Rayleigh(19) developed the first accurate method of studying ripple phenomena; to render visible the very small disturbances of the surface he used a modified form of Foucault's method of testing plane surfaces. Further, he used the stroboscopic method for making the waves appear to stand still.

Reference has been made already to the work of Tyndall and of Vincent, who used ripples to illustrate wave motion. A style attached to a vibrating tuning fork was used to generate the waves. Shultze(20) devised a novel electrical method of producing ripples which Pfund(21) and Palmer(22) have developed further. Waetzmann(23) generated waves by intermittent puffs of air, and Watson and Shewhart,(24) using a modification, obtained some interesting photographs of wave phenomena.

In the present apparatus the waves were generated by means of a style attached to an electrically maintained tuning fork. The ripples were viewed by intermittent flashes of light isoperiodic with the oscillations of the style. The following details of the apparatus may be of interest.

The ripple tank was about 3 ft. by 5 ft. in size, and 2 in. deep, the bottom being of plate glass. For the experiments water was introduced into the tank, usually to a depth of about 2 cms. For the wavelengths used this depth was sufficient to satisfy the requirement $l>\lambda/2$ referred to in establishing the analogy to acoustical propagation and in evaluating the viscosity effect. The style used to agitate the water was a copper wire 0·2 cm. in diameter, with a gently rounded end. Provided the wire was fairly vertical on entering the water, and the tip was just about level with the water surface, excellent ripples were attained, spreading equally in all directions from the source. Excessive amplitudes of vibration of the fork resulted in streaming of the water and distortion of the ripple circles.

---

* Values of wavelength and velocity corresponding to a given frequency are nearly the same for mercury as for water. If the suffix m relate to the wavelength at which the velocity is a minimum, we have in centimetre units the following values for water and for mercury: Water: $\lambda_m=1{\cdot}73$; $c_m=23{\cdot}2$; $n_m=13{\cdot}4$. Mercury: $\lambda_m=1{\cdot}27$; $c_m=19{\cdot}9$; $n_m=15{\cdot}7$. Relations between c/c_m, λ/λ_m and n/n_m are the same for all mobile liquids.

As regards the frequency of the fork, we have seen that the longer the wavelength the less important the viscous damping. However, long waves necessitate large tanks, and in the tank available the lowest frequency used was consequently about 20 vibrations per second. This corresponds to a wavelength of 1·2 cm. Incidentally in this region the group velocity $U=c-\lambda(dc/\partial\lambda)$ differs but little from the wave velocity. To obtain an adequate number of ripples in the tank a higher frequency of 50 per second was usually necessary; this gave approximately half the wavelength associated with the slower fork.

To render the wave visible intermittent light from an electric arc about 10 ft. distant was passed vertically upwards through the glass bottom of the tank, and cast a shadow of the waves upon a horizontal screen suitably mounted about 5 ft. above. The intermittence was secured by means of a stroboscopic sectored disc driven in synchronism with the tuning fork by means of a 10 volt phonic motor. The slots in the discs occupied about one-eighth of the total area, so that during any flash the wave advanced not more than one-eighth of a wavelength. The ripple pattern upon the screen was photographed. By using a translucent screen the pattern could be photographed from above with no fore-shortening. Actually, however, it was photographed from below from the side of tank; distortion was largely corrected by setting the illuminating beam at a slight angle to the vertical, or by using the falling back of the camera.

The height of the screen was chosen to give good definition for waves at a distance from the source, since chief interest was centred in them. No one position is equally satisfactory for all amplitudes. In ripple photographs given later (Figs. 2 and 3) the blurring near the source arises from this choice of screen distance, not from any imperfections of the waves.

There is not necessarily any simple relation between the amplitudes of two unequal ripples, and the optical density of the two corresponding regions in the photograph. In interpreting the subsequent photographs one must in general be content to assume that when two portions of the same photograph are equally intense, they relate to regions of equal wave amplitude.

As will be seen later continuous waves were not always employed. Fig. 1 gives a general view of the ripple tank, and shows a round-headed dipper which was used to generate short pulses. In operation it was merely withdrawn from the water by electromagnetic means; vibrations and consequent splashing were prevented by the brass leaves between which the dipper slides. A model section of a building of which the reflecting characteristics of the outline were required, is shown in the water lying flat upon the glass bottom of the tank. The inclined beach shown to the left of the tank prevents reflections of waves from this end. This property of a beach was pointed out by Dr. Vincent.

Diffraction Measurements.

Experiments were carried out to determine the characteristics of continuous water ripples. In preliminary work some diffraction patterns were studied. Six

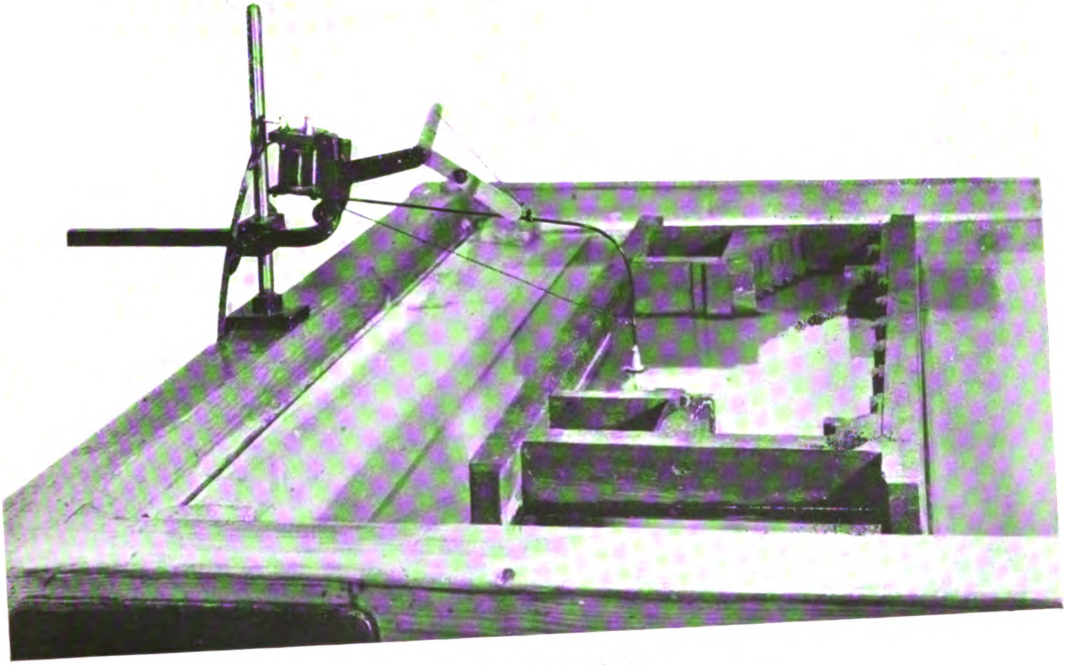


FIG. 1.—RIPPLE TANK.

To face page 240]

UNIV. OF MICH.

points spaced 2 cms. apart, and fixed to a straight bar were carried on a tuning fork, so that all six points agitated the water. An interference pattern was set up, and measurements were made of the directions of the maximum and minima of intensity, with the following result :—

——	1st max.	1st min.	2nd min.	3rd min.	4th min.	5th min.
Theoretical	37°	30°	24°	18°	12°	6°
Observed	36°	32°	25°	16°	10°	Not visible.

The spectra resulting from two diffraction gratings of ten slits were then observed. One grating had slit-widths of 1 cm., the other of 2 cms. In each case the opaque portions of the grating were 1 cm. wide. First order and second order spectra were studied in the two cases, with the following result :—

——	Observed spectra.		Wavelength. Calculated.	Wavelength. Observed.
1st Grating	1st order	22°	0·75	0·86
	2nd order	63°	0·89	
2nd Grating	1st order	15·5°	0·80	0·86
	2nd order	28°	0·70	
	3rd order	53·5°	0·80	

The above measurements* were made on a screen before photographic arrangements were developed. The angles were necessarily measured rather closer to the grating (50λ to 100λ) than is usual in optical experiments. In view of the errors possible under such circumstances the agreement is quite good. The experiments have not been repeated.

Screening by an Obstacle.

In order to study the effect of varying conditions in the ripple tank, photographs were taken under various circumstances of the bending of ripples around a standard obstacle. The obstacle was placed in the tank at a definite distance from the centre of disturbance. Photographs were taken of the distribution of ripples revealed. Observation was made of the intensity of the waves on the photograph at some standard screened position, and measurement was made on the photograph of the distance from the source at which unobstructed ripples attained this same intensity. For each condition tested—fresh or stale water, large or small fork amplitude, etc.—the intensity at a screened position was thus expressed in terms of a distance from an unscreened source. For this work the normal obstacle was 2·5 cms. by 5·9 cms. in size, and the wavelength of the ripples was about 0·6 cm.

Effect of Meniscus around Obstacle.

Experiments were conducted to ascertain whether the water meniscus around the model affected the bending of waves around it. Increasing the size of the obstacle should presumably lessen the importance of any meniscus effect, but when the scale of an experiment was doubled, no appreciable difference was observed.

An attempt was also made to vary the meniscus effect by greasing the model.

---

* I am indebted to Mr. N. Fleming, B.A., for these measurements.

Two types of experiment were conducted. In the first ripple distributions were photographed before and after the model was greased. Generally speaking, there was no appreciable difference, and the maximum deviation observed was an increased intensity at the standard screened position corresponding to a 10 per cent. decrease in distance from an unobstructed source. This type of experiment has the disadvantage that the surface of the liquid is not in the same state for the two photographs. Special photographs were consequently taken in which a source was placed symmetrically with respect to two similar models, one of which had been greased. Fig. 2 shows two such photographs taken with identical disposition of apparatus. In one the left-hand model is greased, and in the other it is the right-hand one. No appreciable difference is visible.

Effect of Amplitude of Fork.

Under various conditions photographs were taken for different values of fork amplitude, avoiding as far as possible amplitudes so excessive as to cause streaming of the water and distortion of the ripple circles. In some cases it is thought that slight distortion did occur. On the average, varying the fork amplitude did not affect relative intensities in different parts of the field : in some cases slightly increased bending was recorded, in others a slight decrease. Variations in relative intensity at the screened position did not exceed that covered by a ±10 per cent. change in distance from an unscreened source.

Effect of Condition of Water Surface.

Fresh clean water gives a larger field of ripples than water which has become dusty, etc., through exposure in the tank for several hours. The reduced amplitudes in the latter case are presumably due to a viscosity effect, consequently they should be associated with an apparent increase of intensity in screened regions as compared with unscreened. For if the intensity appears to be the same at two points, one screened and one unscreened, the screened region is at a smaller path distance from the source, and has undoubtedly suffered less from viscous diminution.

An hourly series of photographs was taken during one day to reveal the extent to which the bending of ripples around an obstacle was affected by the surface contamination referred to. Fig. 3 shows four photographs covering an interval of twenty-four hours. On each photograph of an identical set of prints two standard screened positions, A and B, were marked, and measurements were made of the distances at which unobstructed ripples appeared to reach the intensities at these standard positions. Table II summarises results as estimated :—

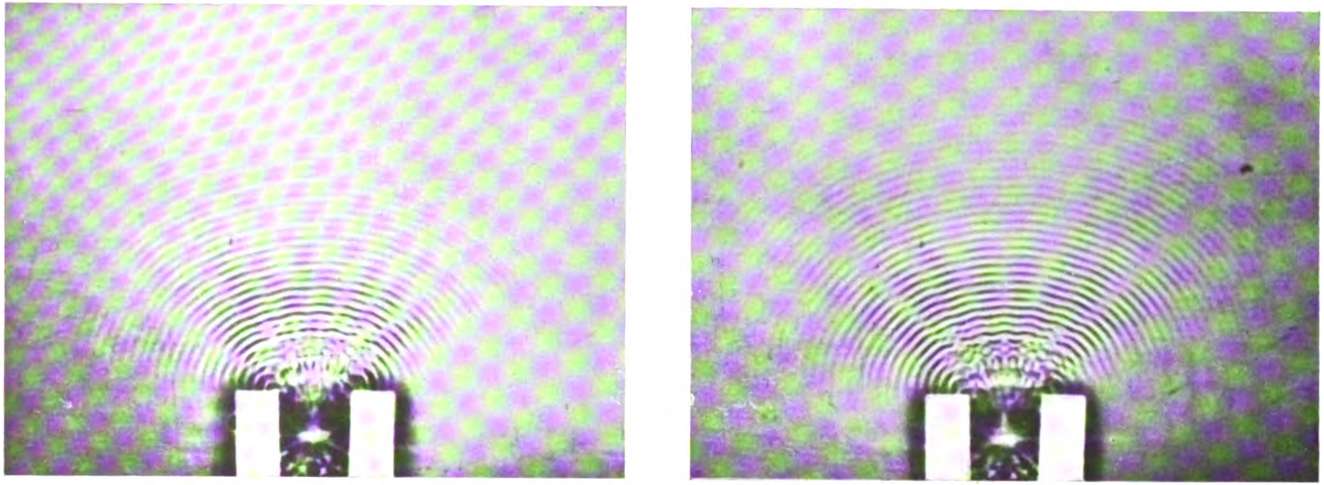
TABLE II.—*Effect of Exposure of Water Surface.*

Time in Hours.	Distance at which unobstructed ripples reach the intensity of the standard screened positions (wavelengths).	
	A	B
0	—	47
4	42	28
7	32	23
24	30	25

The standard positions A and B were at path distances from the source of $21 \cdot 3\lambda$ and $16 \cdot 3\lambda$ respectively. The wavelength did not alter with time. In the

UNIV. OF MICH.

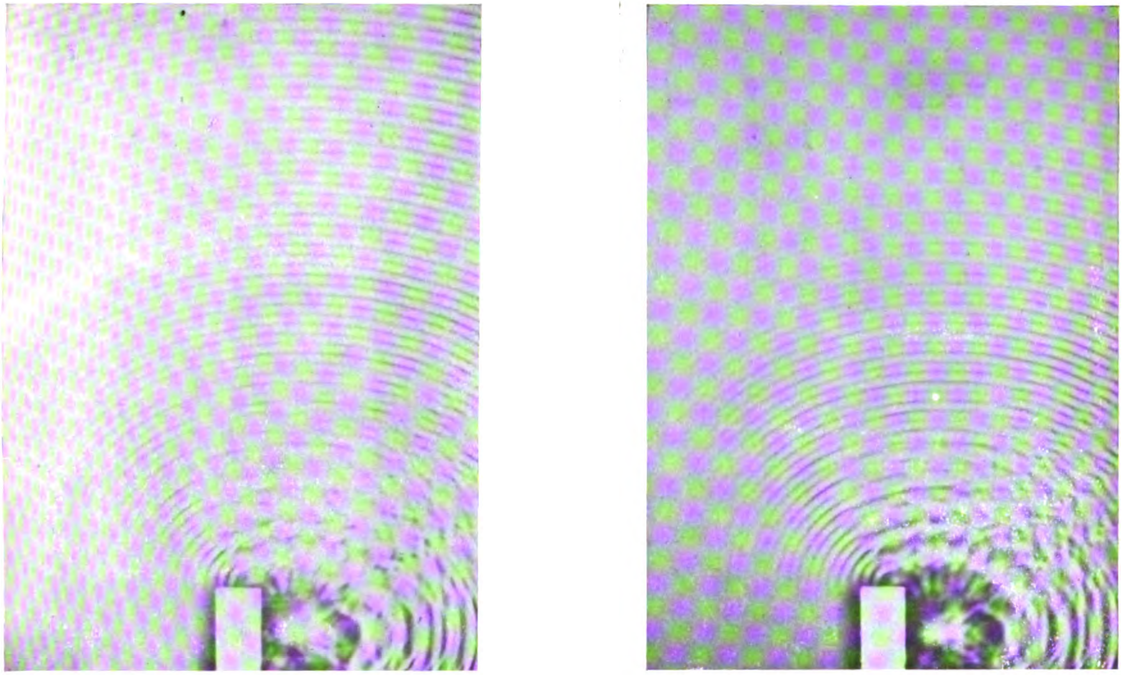
To face page 242]



Left-hand Model greased.

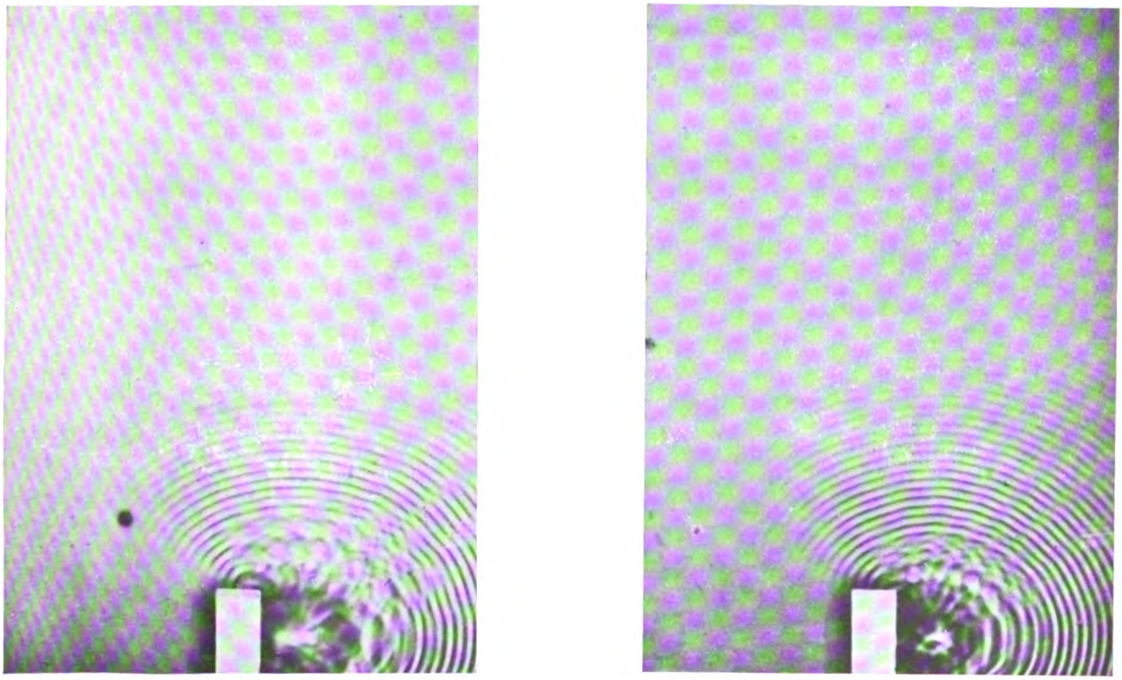
Right-hand Model greased.

FIG. 2.—EFFECT OF GREASING MODEL.



0 Hours.

4 Hours.



7 Hours.

24 Hours.

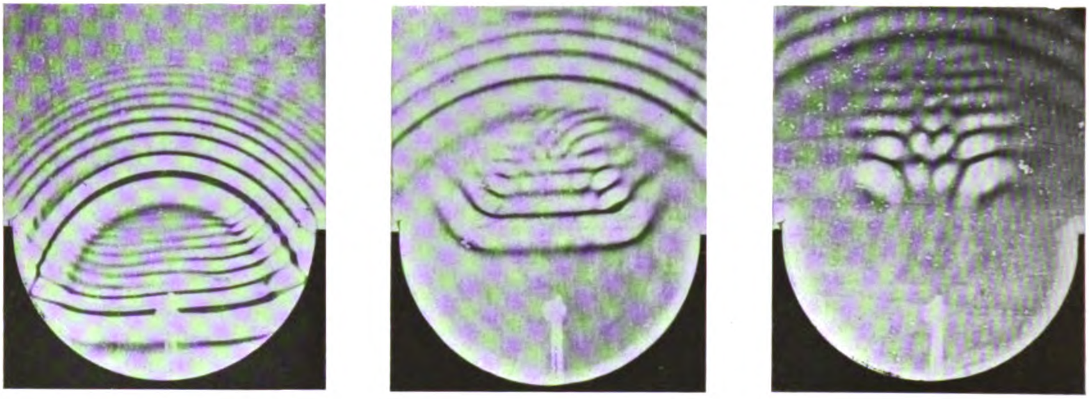
FIG. 3.—EFFECT OF EXPOSURE OF SURFACE OF WATER.

To face page 242]

UNIV. OF MICH.

UNIV. OF MICH.

Ripples.



Sound Pulse.

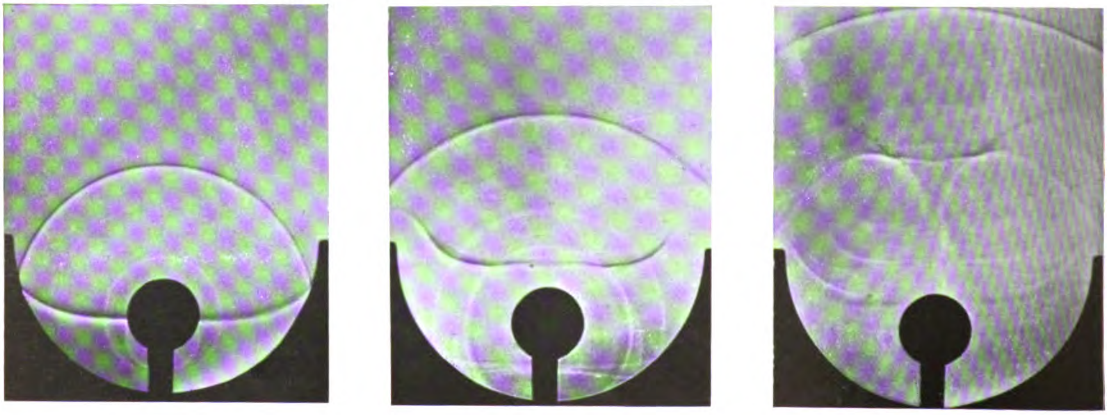


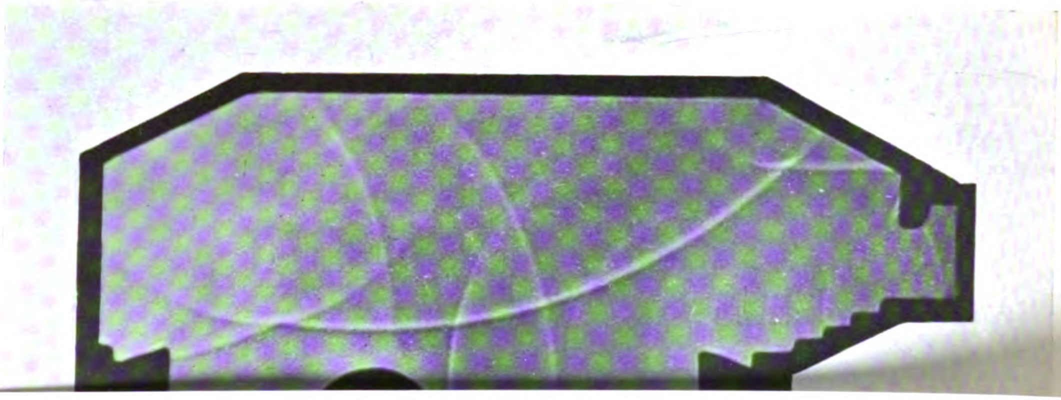
FIG. 4.—COMPARISON BETWEEN RIPPLE AND SOUND PULSE PHOTOGRAPHS RELATING TO REFLECTION FROM A HEMICYLINDRICAL MIRROR.

[*To face page* **243**

UNIV. OF MICH.

of zone plates or diffraction gratings, etc., or to architects the reflecting characteristics of the boundaries of a proposed building.

SOUND PULSE PHOTOGRAPH.



UNIV. OF MICH.

extreme case of very stale water, the apparent bending of ripples is appreciably increased, for unobstructed ripples reach the intensity of the standard screened positions in about one half the distance required with fresh water.

From theoretical considerations, we have seen that even for fresh water appreciable viscous decay of ripples will occur. The present experiments show that when the surface is exposed to the air of the room its apparent viscosity increases after a few hours. Consequently relative intensity measurements are somewhat unreliable for points having markedly different distances from the source. No indications have been given, however, that the intensity relations from point to point along a wave front are altered by viscous effects.

Wave Pulses.

So far discussion has been confined to the case of harmonic waves continuously maintained, for which the analogy between surface waves and sound waves is seen from the appropriate equations to be so close. In studying the directions in which parts of a wave front are reflected or diffracted—a problem which arises for instance in dealing with acoustics of buildings—it is much more convenient to trace the history of a single pulse or short train of waves than to attempt to interpret the complicated wave pattern which would arise from the use of continuous waves. In some respects ripples and sound waves differ in behaviour when pulses are concerned. A sound pulse travels out singly, but in the case of an impulsive disturbance of a water surface a number of smaller ripples travel in front of the main pulse. In spite of these differences—which would greatly complicate the equations of the analogy—both are essentially wave motions of a more or less impulsive type, and some close correspondence in behaviour is to be expected.

Fig. 4 compares results obtained by means of the ripple tank with some actual sound-pulse photographs obtained by the Toepler-Boys-Foley method. Both relate to a disturbance due to a source at the focus of a hemicylindrical mirror. The photographs have been taken at approximately equivalent time intervals after the origin of the wave. They show the outgoing circular part of the wave front and also the part which has been reflected from the mirror. In each case the reflected part is seen to be a plane wave modified at its extremities by spherical aberration.

In Fig. 5, photographs (*a*) and (*b*) compare ripple and sound-pulse photographs relating to the behaviour of waves after reflection from boundaries representing the longitudinal section of a hypothetical council chamber. The ceiling is at the top of the photograph, and extends over the galleries at each end. The position of the speaker—indicated by the large black circle in the sound-pulse photograph—is practically the same in both cases, and the distances travelled by the waves correspond almost exactly. The sound-pulse photograph is clearer because it deals with only a single pulse instead of a short train of waves, but when this is recognised the correspondence between the two photographs is most striking, not only as regards the main ceiling reflection, but as regards the extent and direction of reflections from subsidiary surfaces.

Illustrative Uses of a Ripple Tank.

The use of a ripple tank is mainly to demonstrate the propagation of waves in certain cases. It may be used to demonstrate to students and others the behaviour of zone plates or diffraction gratings, etc., or to architects the reflecting characteristics of the boundaries of a proposed building.

In Fig. 5, photographs (*b*) and (*c*) illustrate an application to the study of the acoustics of buildings. They show the desirability of putting the gallery under the main ceiling of the council chamber concerned. If ceilings are low enough, they do not give rise to distinguishable echoes; indeed, reflections of sound from them contribute usefully in raising the level of loudness in regions reached. Ceiling reflection is particularly desirable in large council chambers where speeches may be delivered from any part of the floor, for no other reflecting surface would be equally effective for all speakers. In the photograph 5(*b*) we see the ceiling reflection spreading to benefit people even in the rear of the right-hand gallery; in 5(*c*), where the roof has been modified so that the gallery is under a separate ceiling, this useful reflection to the back is cut off.

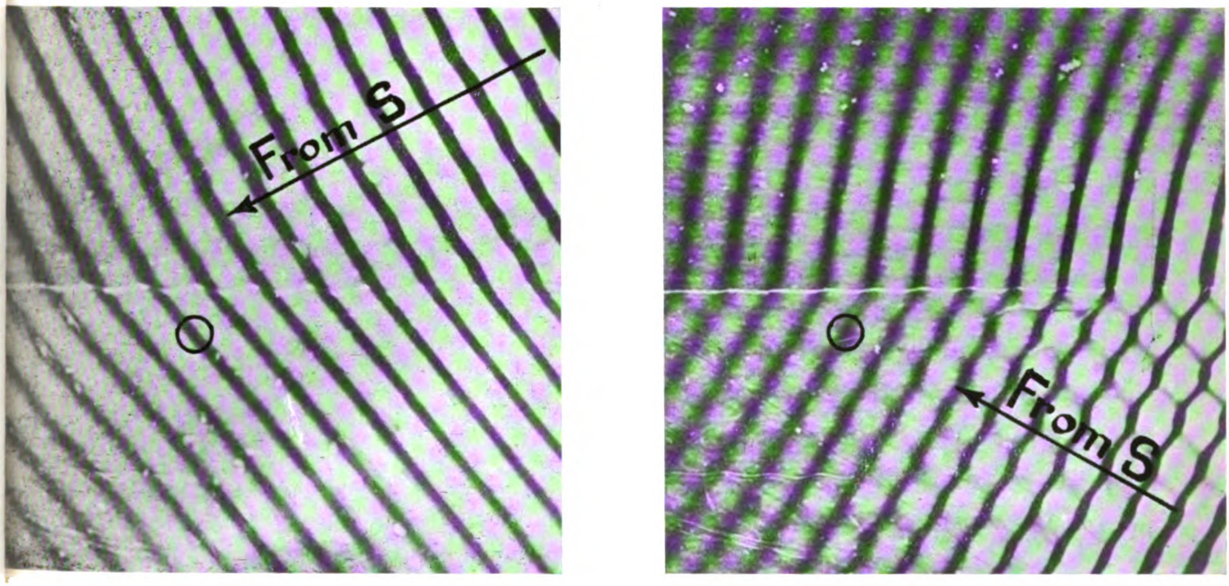
Figs. 2 and 3 illustrate a case of screening on a scale which might arise with a source of sound near a building or buildings in the open air. In this case the analogy must not be pushed too far, for we have seen that the viscosity of the water affects the apparent screening. However, very considerable changes of sound intensity are necessary to modify in any marked manner the sensation of loudness, and cases may well arise in which the moderate differences arising from viscosity are not important.

The final photograph, Fig. 6, illustrates certain simple wave phenomena at a boundary that may lead to error in the apparent bearing of the source. It is of interest in connection with errors in direction-finding by wireless waves as observed at a station near the sea coast.(25) Conditions corresponding to any change of velocity of waves on crossing the boundary were attained by providing one-half of the tank with a false bottom only slightly submerged. In the photographs the boundary is clearly apparent. The direction of the source S has been indicated by an arrow, and a point O has been marked to represent the position of an observing station. In Fig. 6(*a*), which relates to the case of a source and observing station on opposite sides of a boundary, the apparent direction change is evident. In Fig. 6(*b*), where source and observing station are both on the low-velocity side of the boundary, the condition at the observing station is seen to be complicated by the presence of the internally reflected wave. In both cases the apparent bearing of the source lies further towards the top of the page than its true position.

The author desires to thank Mr. N. Fleming, B.A., for his assistance referred to in the text and in connexion with the sound-pulse equipment and technique. Mr. R. Berry, Junior Observer, assisted with the experiments and photographs.

REFERENCES.

(1) Tyndall. *See* S. P. Thomson, " Light, Visible and Invisible," Chap. I.
(2) Vincent. Phil. Mag., 43, p. 17, 1897; 45, p. 191, 1898.
(3) Watson. "Acoustics of Buildings," p. 12. Wiley & Sons, 1923.
(4) Michel. "Hörsamkeit grosser Räume." F. Vieweg & Sohn, 1921.
(5) Scott Russell. Brit. Ass. Report, p. 96, 1843.
(6) Scott Russell. B. A. Report, p. 331, 1844.
(7) Lamb. "Hydrodynamics," 5th ed., Arts. 189, 172. Camb. Univ. Press, 1924.
(8) Lamb, loc. cit., Art. 287.
Rayleigh. "Theory of Sound," 2nd ed., Art. 273. Macmillan & Co., Ltd., 1896.
(9) Lamb. Loc. cit., Art. 288.



(a) (b)

FIG. 6.—WAVE PHENOMENA NEAR A REFRACTING BOUNDARY

To face page 244]

U. OF MICH.

(10) Lamb. Loc. cit., Art. 257.
(11) cf. Rayleigh. Loc. cit., Art. 353.
(12) Lamb. Loc. cit., Arts. 302-305.
(13) Stokes. Math. & Phys. Papers. Camb. Univ. Press, 1, p. 100, 1880.
(14) Lamb. "Dynamical Theory of Sound," 2nd ed., Art. 64. Arnold & Co., 1925.
(15) Lamb. "Hydrodynamics," Art. 359.
(16) Kirchhoff. Pogg. Ann., 134, p. 177, 1868. (See Lamb, "Dynamical Theory of Sound," Art. 65.)
(17) Lamb. Loc. cit., Art. 348.
(18) Lamb. Loc. cit., Art. 351.
(19) Rayleigh. Collected Papers, 3, p. 383.
(20) Shultze. Zeits f. Instk., p. 151, 1907.
(21) Pfund. Phys. Rev., 32, p. 324, 1911.
(22) Palmer. Phys. Rev., 33, p. 528, 1911.
(23) Waetzmann. Phys. Zeits, 12, p. 866, 1911.
(24) Watson and Shewhart. Phys. Rev., 7, p. 226, 1916.
(25) Smith-Rose. Nature, 116, p. 426. 1925.

DEMONSTRATION.

The author, assisted by Mr. Berry, illustrated the Paper with a demonstration in which (*a*) continuously emitted ripples were viewed stroboscopically under conditions illustrating refraction and also diffraction by a grating, round a screen, and through apertures of various sizes; and (*b*) single pulses, internally reflected within a wooden enclosure, representing the vertical section of an auditorium and laid in the ripple tank, were viewed by instantaneous illumination.

DISCUSSION.

Major W. S. TUCKER said that the Author had described an elegant method for solving practical acoustic questions which it would be difficult or impossible to handle mathematically. In the neighbourhood of aerodromes great inconvenience was caused by the noise made by the running up of engines before flight. The author had attacked this problem, at Major Tucker's request, by means of a model illustrating the screening due to a hangar, the wavelength employed being produced to scale, and the ratios of the intensities at various points in the shadow being estimated as described in the Paper. The speaker exhibited some of the photographs obtained in this connexion. It must be borne in mind, however, that the two-dimensional solutions given by the Paper do not necessarily give safe guidance in the case of three-dimensional problems. The speaker illustrated this point by a further slide, showing by polar diagrams the calculated distribution of intensity in the neighbourhood of a sound source screened by placing it (*a*) midway between two parallel plates and (*b*) inside a tube of diameter equal to the distance between the plates, so that the two systems are identical in section. In this extreme case two entirely different sound distributions are obtained.

Dr. J. H. VINCENT congratulated the Author on his learned and delightful Paper. He would have thought that, for all purposes except refraction experiments, a reflecting surface like that of mercury would have been preferable to the water surface actually used. The meniscus effect at the edges of a screen can in a mercury tank be eliminated by making the screen of thin cover glass and allowing it to float on the mercury. For refraction effects mercury is unsuitable, however, because on account of the cost of the metal the dimensions of the apparatus have to be small, and the reduction of depth necessary to exhibit refraction effects cannot be achieved because of the tendency of mercury to gather into drops of a certain minimum depth on a surface which it does not wet. Amalgamated submerged surfaces have therefore to be used as screens, and their position cannot conveniently be photographed.

Mr. E. G. RICHARDSON said that the impulse method seemed to him more satisfactory than the ripple method for studying the acoustics of buildings, and it had, he believed, been more extensively used by Sabine for that purpose. In filming plays in which wrecks occur it used to be the practice to photograph a sinking model boat, but usually no attention was paid to the scale of the ripples, with the result that the waves seen were sometimes longer than the boat. The method of scaling adopted by the author would have been useful in such cases, but it appeared to be the practice, under the financial conditions which now obtain in America, to sink full-size vessels.

Mr. M. D. HART said that the author spoke in the second paragraph of his Paper of the value of "ripples in a *small* tank," but would not experiments on a larger scale be more satisfactory? He would like to ask how the measurement of the ratios of the intensities in different regions of a sound shadow were carried out.

AUTHOR'S reply: I naturally agree with Major Tucker that two dimensional solutions of acoustic problems have limitations; indeed, in stating that the strict analogy is between ripples and cylindrical sound waves, some limitations to general use are implied. Particularly caution must be observed where interference phenomena are prominently involved, as in the special cases quoted by Major Tucker. However, ripple tank results appear to be useful, for instance, in connection with the acoustics of buildings of not too complicated shape. Here it is desired to ensure that the shape of a section shall tend to reflect sound to certain regions rather than to others; the question of the interferences which may arise in regions reached by the sound is of subsidiary importance and probably where articulate speech is concerned of no importance at all. With respect to the size of the tank, a larger one would be advantageous for reasons indicated in the Paper, but would be somewhat unwieldy. The present tank is quite large enough to deal with model sections of buildings on a scale of ¼ in. to 1 ft., and on this scale the distance from crest to crest between successive ripples in the impulsive train corresponds to sounds having a frequency of 200-700 per second, a region in the speech range. Dr. Vincent's remarks on the use of mercury are very interesting. It should be noted that the use of mercury does not greatly alter the wavelength-velocity-frequency relations, but for a given degree of damping a wavelength may be used of about one-third of that required with water. Thus relatively large tanks may still be desirable, and one must decide in any case whether the convenience and cheapness of clean water do not justify its adoption. The models were photographed in position after removing the water, in order to avoid blurred outlines; the same method might be employed in a mercury bath having amalgamated submerged models, of the kind mentioned by Dr. Vincent. When ripples are studied instead of sound pulses, the complete progress of waves may be observed visually or followed in detail by the kinema camera; further, modifications of the model may be studied rapidly by adjusting the position of loose parts. For photographic presentation of results sound pulse photography is much clearer. Intensity distributions in a shadow may be studied by judging by eye at what distance from the source in the unscreened region of the photograph, the photographic intensity of the ripples is the same as that at any given screened point.

XXVII.—ON THE EVAPORATIVE LOSSES OF VACUUM-JACKETED VESSELS OF THE DEWAR TYPE.

By R. M. Archer, *A.R.C.Sc., B.Sc., M.I.E.E.*

Received February 4, 1926.

Abstract.

In this Paper the evaporative losses of metal Dewar vessels are discussed, and particulars given of experiments made by the author in Oxygen Laboratory of the Air Ministry. The separation of neck and radiation losses is described, and also a method of testing adsorbents under working conditions. Experimental details are given with graphs and tables.

Introduction.

VERY little information regarding the vacuum-jacketed Dewar flask was obtainable until 1918, apart from that given in a few Papers by Professor Dewar himself, and some structural details derived from examination of vessels of foreign make. Towards the end of that year certain monographs prepared by the late Dr. Harker and his associates were available in the Oxygen Laboratory of the Air Ministry, and were published subsequently in an abridged form by the Oxygen Committee of the Department of Scientific and Industrial Research. These Papers dealt mainly with the theory of vacuum flasks and other heat-insulated vessels, but the need of improving existing types and of working out methods of evacuating them in bulk is mentioned also. The importance of testing the performance and characteristics of glass and metal vacuum flasks and of drawing up specifications is pointed out, and it is stated that " at present complete data concerning any one vessel are lacking." The action of the adsorbent is only considered very briefly in the monographs, and no reference is made to the difficulty of removing gases from it and from the walls of the vessel, nor to the rise of pressure and evaporative rate which occurs after long use.

In October, 1918, the author had occasion to report upon the adsorptive power of activated charcoal and devised simple apparatus for making a preliminary examination. A large burette containing the dry gas under test (usually air) was connected at the bottom to a movable mercury reservoir, and at the top to a small bulb of the adsorbent, which could be immersed in water or in liquid oxygen. Allowance having been made for the contraction of the gas in the unfilled part of the bulb (by making a dummy experiment with the bulb partially filled with a non-adsorbent) the volume of gas taken up at atmospheric pressure, and in some cases, at reduced pressure, was found ; and in the report the need for making measurements at very low pressures was emphasised. Samples of wood and fruit stone-charcoal were examined, and their apparent density found ; and somewhat later tests were made with precipitated copper, copper oxide, pumice, fine sand, pith, lycopodium, and other substances.

The method of testing the adsorbent under working conditions which is described in this Paper is based upon the general experience of the Air Ministry Oxygen Laboratory in 1918 and the first half of 1919 ; but the author in 1920, when working out details of bulk evacuation and leak testing, found it desirable to include long period tests (taken after sealing), and in some cases to put the adsorbent into an external metal capsule, and to connect vessels in parallel while under examination.

Also, the use of a sensitive reflecting flowmeter was found subsequently to be necessary in special cases.

In the calculation of neck losses given in the Harker monographs no account was taken of the cooling action of the vaporised oxygen.

Banneitz, Rhein and Kurze, in a comprehensive Paper on vacuum flasks,* refer to this action, but state that in certain experiments they made the results were inconclusive. Briggs, in a Paper on the Dewar vessel,† describes experiments made on temperature gradients in the inner necks, and mentions some early tests on containers with short necks. Temperature gradients are mentioned also by Griffiths,‡ Hagen and Rubens,§ in Papers published in 1900 and later, drew attention to the influence of wavelength and of temperature on the reflecting power of various surfaces, and showed that in certain cases, an increase in wavelength may cause the reflecting power of two surfaces to become more nearly equal. (Thus a change of wavelength from 450 $\mu\mu$ to 700 $\mu\mu$ increased the amount of radiation reflected from silver in the ratio $\frac{94\cdot6}{90\cdot6}$, the corresponding ratio for copper being $\frac{90\cdot7}{48\cdot8}$.)

Harker and Groom, in the Papers previously mentioned, state that reflecting powers of surfaces vary in a very irregular way with the wavelength. " Values of emissivity, deduced from determination of the reflecting power made under normal conditions have little validity, when applied directly to the conditions obtaining in the vacuum flask."

They point out that direct determinations for long waves are very difficult, and that relative measurements by experiments on flasks " suffer from the disability that it is difficult to disentangle the effects of pure radiation from those of conduction." In consequence of uncertainty as to the correct values under working conditions they use, in their examples, " best " and " probable " values, and values deduced by theory from a knowledge of electric conductivity. As in the design of vacuum flasks a knowledge of the normal gas conduction, radiation and neck losses is required, and estimation of the effect of dust, oxide, solder, and defective polishing on the radiation losses is of great practical importance, determinations under working conditions are essential.

In the present Paper experimental data relating to a number of standard vacuum-jacketed metal vessels have been given, and the aim of the methods described has been to find a solution of the problem of " disentangling " experimentally all the chief sources of loss.

The author would like to take this opportunity of thanking the Air Ministry and the Department of Scientific and Industrial Research for leave to publish the information given in this Paper.

---

* " Investigations with Regard to the Principles of Construction of Containers for the Transport of Liquid Gases," (translation) Annalen der Physik, 4th Series, Vol. 61 (1920).

† " An Experimental Analysis of the Losses by Evaporation of Liquid Air contained in Vacuum Flasks," Proc. Roy. Soc. Edinburgh, Vol. 41, Pt. 2, No. 10 (1921).

‡ Trans. Faraday Society, 18, Dec. 1922, p. 230.

§ Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraph 37, Table IV.

I. SOURCES OF LOSS.

Since the rate of evaporation of the cold liquid in a Dewar vessel depends upon the rate at which heat reaches it, an experimental determination of the efficiency of the flask should include a measurement of the individual losses due to the entry of heat by each of the principal routes. The chief losses are due to :—

(*a*) Conduction along the material of the inner neck.

(*b*) Conduction through the residual gases in the space between the envelopes or shells.

(*c*) Convection in these residual gases.

(*d*) Conduction and convection in the vapour above the liquid.

(*e*) Radiation between the opposing surfaces of the shells.

(*f*) Radiation through the aperture of the inner neck.

In metallic vessels of normal proportions the inner neck, which is usually of nickel-silver or cupro-nickel, is long and narrow, and the error due to neglecting (*f*) is small. Convection in the residual gases is negligible also even in a vessel which has been evacuated only moderately. As regards the vapour itself the chief effect to consider is its abstraction of heat from the inner neck. This action makes it difficult to find either experimentally or by calculation, the net amount of heat which reaches the liquid by conduction down the neck.

In this Paper it is assumed that the vessels are of normal type, and that under normal conditions heat can reach the liquid in the following ways only :—

A. By conduction across the residual gases.

B. By radiation between the envelopes.

C. By conduction through the substances of the inner neck (cooling action of vapour taken into account). The losses dealt with under this heading are called " neck losses."

A and B are practically independent of one another and of C. But C is a function of A and B.

The method of evaluating the losses, which will now be described, has been applied to vessels of 25, 5, 3 and 1 litre capacity, and has yielded also some useful information regarding the vacuum-improving power of certain adsorbents.

II. APPARATUS AND PROCEDURE.

(A) *Apparatus*.

The vacuum flask *A*, Fig. 1, is placed in a water bath and the space between the envelopes connected to an evacuating system by a metal pipe, a special vacuum joint *U* being made between the metal and the glass parts of the system. Connected to the system is a large McLeod gauge *K*, an Anschütz gauge *I*, with a special air trap,* a tube *H* of activated charcoal, a gas-injection apparatus *L*, and a mercury seal *J* controlled by a movable reservoir of mercury. High vacuum taps *P*, *Q*, *R*, *S* and *T* are provided, and there are air traps at *X* and *Y*. Accessory glass apparatus such as drying tubes may be blown on to the blind tubes *F*, *M*, *N*, *O*, *V* if required. The system may be evacuated by a motor-driven " oil " or " mercury " pump connected below *S*, or by the charcoal bulb in the well-known way. If *P* is closed

---

* "A Simple Regenerative Vacuum Device and some of its Applications," H. P. Waran, Proc. Phys. Soc., London, Vol. 35, Part 4, June 15 (1923).

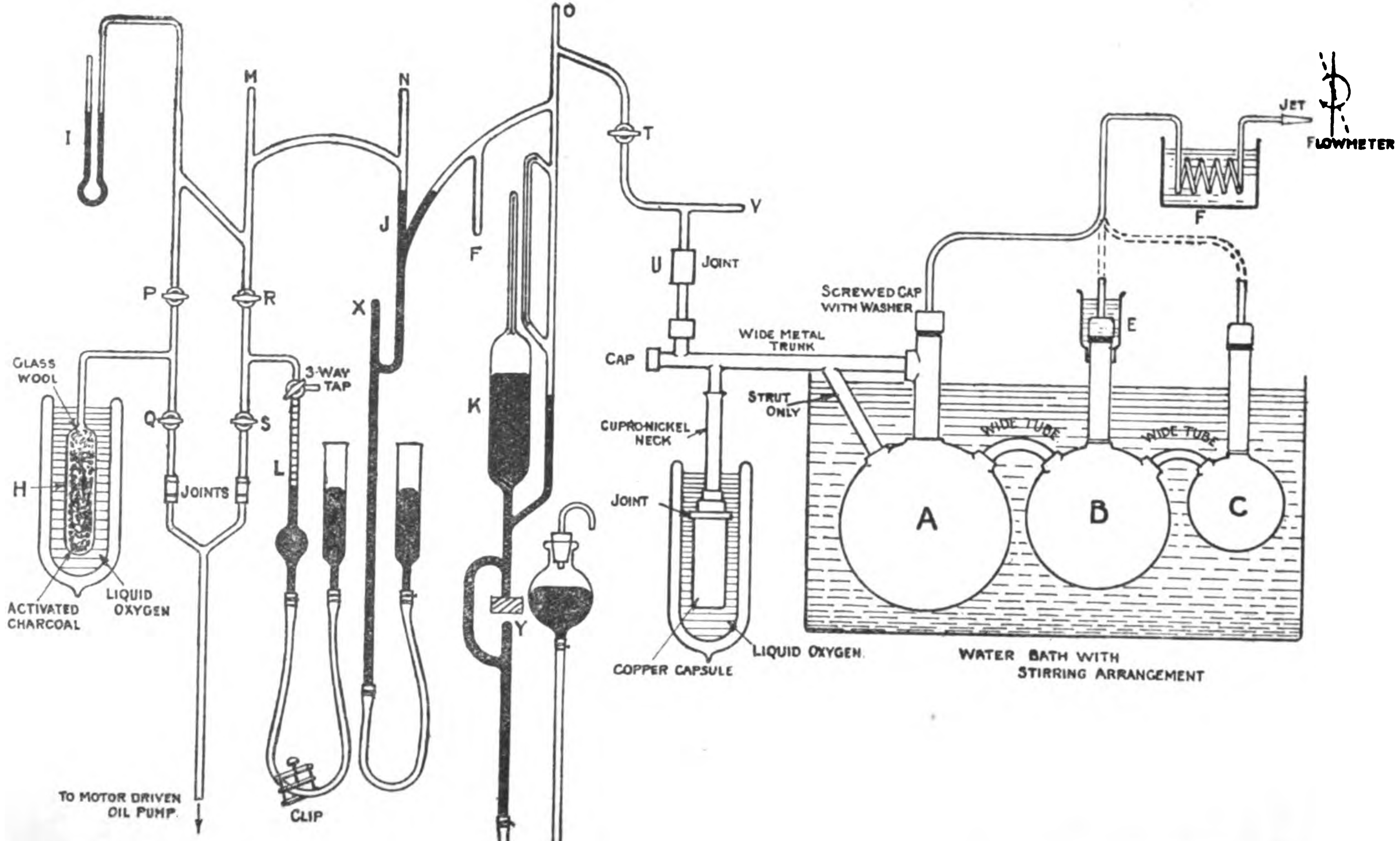


FIG. 1.—GENERAL ARRANGEMENT, SHOWING EVACUATION PLANT AND DEWAR VESSELS UNDER TEST.

and Q opened the charcoal may be out-gassed without interfering with the rest of the evacuating system.

In some experiments the adsorbent to be used in the Dewar flask itself is placed in its usual position in the internal cup, but this is not always done when it is necessary to vary its amount or to replace it by another one. Removal and replacement of the outer copper envelope of a normal flask would involve repolishing the reflecting surfaces, and might alter the constants of the vessel. Also much time would be lost and the conditions might change appreciably. In such experiments the adsorbent is placed in an external metal capsule (Figs. 1 and 2), which may be opened and closed quickly and easily by using an annular soldered joint. The capsule, which is fitted with a dust filter, has a long nickel silver neck, and may be heated strongly, or may be cooled by liquid oxygen. It is easy to insert or remove the adsorbent without disconnecting the flask from the system or moving the bath. Further, the flask and its capsule may be sealed permanently, removed as one unit and tested independently.

When a comparison has to be made between different flasks they are sometimes connected together by short wide pipes and tested simultaneously, as at A, B and C, Fig. 1. This is better than testing them independently. Equality of pressure is secured, and the residual gases have the same composition, and therefore the same thermal conductivity in all the vessels.

In prolonged experiments, a trap immersed in liquid oxygen may be placed between the flask and the plant to prevent the deposition of mercury on the cold metal surfaces, with alteration of emissivity. (Hughes and Poindexter have shown recently that sodium or potassium may be used for intercepting mercury vapour.)[*]

In determining neck and radiation losses an electrical heater and other special apparatus is used.

(B) *General Method of Experimenting.*

(1) The space between the two envelopes is evacuated well, and the rate of evaporation of the cold liquid measured.

(2) Air or other gas is then admitted to the evacuated space in successive small charges of known amount. The initial and final effect of these injections on the pressure and rate of evaporation is measured.

(3) The changes of pressure produced by these injections when the vessel contains no cold liquid, or when it is heated, is measured also.

(4) In some cases the amount and nature of the adsorbent is varied.

(5) A sample of the adsorbent is placed in a separate glass vessel and its pressure-reducing power when cooled by liquid oxygen found. This experiment is conducted (*a*) at constant (atmospheric) pressure, (*b*) in a closed chamber in which the initial pressure is low, and the final pressure is of the same order as that in a Dewar vessel.

(6) Experiments are made for the determination of the neck and radiation losses.

(7) The flask is sealed and is filled and tested at short intervals over a long period—say once a fortnight for a year or more. The gradual rise in the rate of evaporation serves as a final check on the efficiency of the adsorbent and on the

---

[*] "Potassium as a Mercury Vapour Trap," Phil. Mag., Vol. 50, August, 1925, No. 276. (From Washington University, St. Louis, U.S.A.)

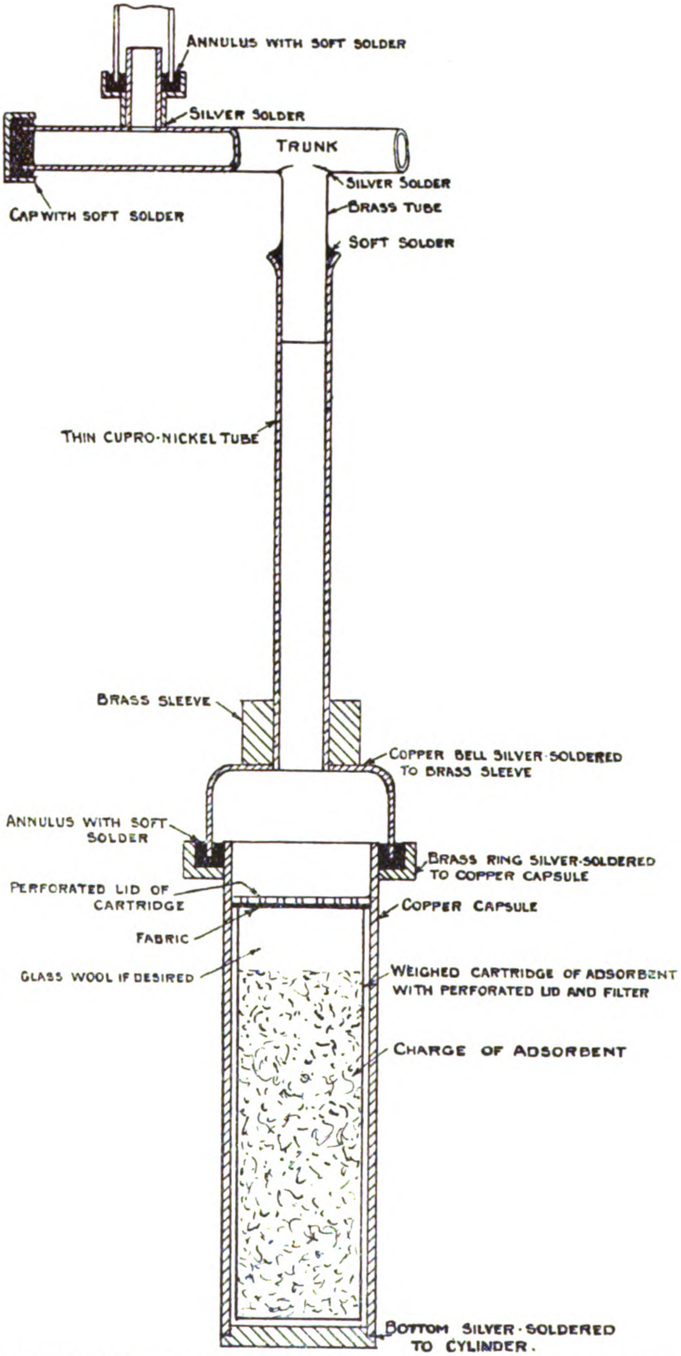


FIG. 2.—DETAIL OF CAPSULE D. EVAPORATIVE LOSSES IN VACUUM-JACKETED VESSELS OF THE DEWAR TYPE.

soundness of the vessel itself. If no formal adsorbent is used, a better measure of the rate of accumulation of gases is obtained; but the metal walls themselves appear to act as adsorbents to some extent.

(C) *Procedure in Specific Cases.*

(1) *Evacuation.*—The vessel was heated both internally and externally during evacuation, and drying was accelerated by phosphorus pentoxide. Evacuation was carried out by an oil pump or mercury pump, and was usually completed by a charcoal bulb in liquid oxygen. It was continued until the pressure was very low, and rose at a very small rate when the flask was isolated. (Full details are given in the Report of the Oxygen Committee, Department of Scientific and Industrial Research, 1923, §§171 to 202.)

In a few special cases the evacuated space was washed out by admitting oxygen gas and re-evacuating a few times, a process suggested by Dewar for removing residual gases not easily adsorbed by charcoal.

After evacuation the container was allowed to cool and the bath was placed in position. Liquid oxygen was then poured into the container and measurements of the rate of evaporation made. Simultaneous readings of the McLeod gauge were taken also. Observations were continued until the rates of change of the quantities became negligibly small.

In certain experiments on a container in 1920 the charcoal was very moist, and to avoid having to open the vessel vacuum distillation was used for removing the water. The rate at which water collected in a glass receiver gave some indication of the rate at which drying was proceeding. Use was made of a manometer also.

(2) *Observations.*—When the rate of evaporation had become constant, a small volume of dry air was drawn into the burette, and its volume at atmospheric pressure measured. It was then allowed to enter the evacuated system, and readings were taken as before, until the rate of evaporation had again become constant. As the volume of the evacuated space was known the amount of air which had entered the container could be calculated. Injections were continued to any desired extent, and in some cases the system was opened finally to the atmosphere.

The vacuum-improving power of the adsorbent was found by comparing the pressures of the residual gases when all parts of the vessel were at one temperature (say 15°C.) with the pressure when the inner shell held liquid oxygen. This was done in one of two ways:—

(*a*) After evacuation had been carried to any desired extent (say until the pressure, after cutting off the pump, remained steady at 10 mm., the temperature being 15°C.) liquid oxygen was introduced, and the steady values of the pressure and the rate of evaporation were noted.

Or

(*b*) When the rate of evaporation of the liquid became steady after a known amount of gas had been injected, the pressure was measured and the liquid oxygen was removed.

All parts of the vessel were then brought up to any desired temperature—usually that of the atmosphere, or that reached during evacuation—and the steady value of the pressure measured.

An advantage of method (*b*) is that the amount of gas held by the adsorbent is known. It might have been calculated in case (*a*), but some assumption regarding the activity of the adsorbent would have had to be made.

Method (*a*) has the advantage that the order of the operations is the same as that followed during the evacuation of a container.

It is not always safe to assume that the order is immaterial, because hot copper gives up gases when heated, and occlusion appears to be slow and incomplete on cooling.

Equilibrium is not usually attained quickly. Charcoal evolves gases for many days when in an evacuated vessel, and observations over such periods are seldom practicable. All that can be done is to wait until the rates of change are small.

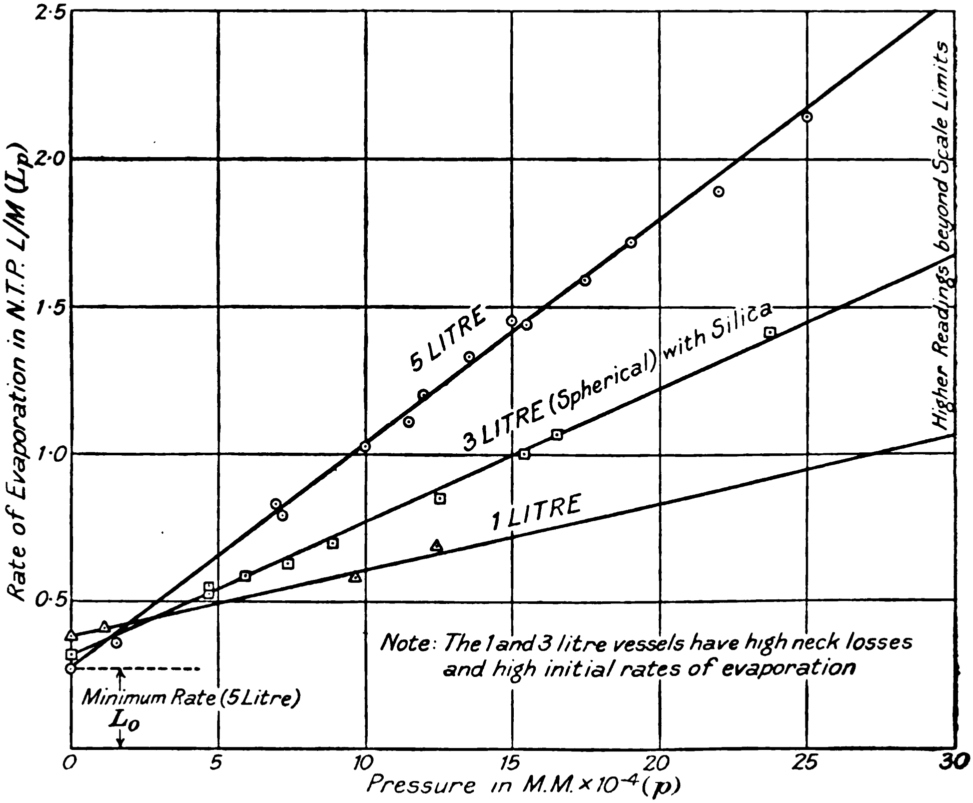


Fig. 3.—1, 3 and 5 Litre Copper Containers with Charcoal Adsorbent or Silica. Variation of Evaporative Rate with Pressure p.

III. General Relationships and Observations.

(A) *Relation between the rate of evaporation of the cold liquid and the pressure of the residual gases.*

The relationship found for a 5-litre copper container examined in 1919 is shown in Fig. 3. After evacuation the rate of evaporation was measured and is regarded here as the minimum attainable. The corresponding pressure was too small to be shown on the scale of the diagram. Known amounts of dry air were then admitted and the corresponding pressures and rates measured. The graph is nearly a straight line, so that the following equation is approximately true.

$$L_p = L_0 + Kp. \qquad (1)$$

where p=pressure of residual gases when the vessel is in use (adsorbent very cold)
L_p=rate of evaporation at pressure p
L_0=minimum rate of evaporation
K=a constant.

Since $K = \frac{L_p - L_0}{p}$ it is numerically equal to the change in the rate of evaporation per unit change in pressure. The values actually obtained in the experiment were :

L_0=0·275 litres of gas per minute (N.T.P.)

K=0·0766 litres per minute per change of pressure of $\frac{1}{10{,}000}$ mm. mercury.

Hence $$L_p = 0{\cdot}275 + 0{\cdot}0766\, p \qquad (2)$$

where p is in mm. $\times 10^{-4}$.

The linear form of the equation, in conjunction with the known laws of gas conductivity, gives an explanation of the facts observed. At the lower pressures reached in the experiment the M.F.P. is comformable with the distance between the envelopes, and over the range tested the conductivity of the residual gas is approximately proportional to p. When p is very low the amount of heat transferred by gaseous conduction is small, and practically the only thermal input is that due to radiation and to neck conduction. It is of interest to find whether the observed increase in the rate of evaporation when gas is admitted agrees with the calculated increase.

Let R=the loss due to radiation, in litres per minute.
N=the loss due to neck conduction in litres per minute, assumed constant for all values of L_p
G=the loss due to gas conduction at pressure p, in litres per minute
H=number of calories conducted through the gas per second
M=mass of liquid evaporated by H calories
p=pressure due to the gas admitted in mm. mercury
θ_1=temperature of the inner (cold) envelope (=91°C. absolute)
θ_2=temperature of the outer (warm) envelope (=292°C. absolute)
A=area of the inner envelope (=1,725 sq. cm.).

Then $$H = Cp\ (\theta_2 - \theta_1)\, A \qquad (3)$$

where C is a numerical factor which is independent of the pressure and has a mean value which depends upon the temperatures of the envelopes.*

Also $$L_0 = R + N \qquad (4)$$

C may be taken as about equal to $2{\cdot}7 \times 10^{-5}$, the unit of pressure being 0·01 mm. mercury.

---

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 23/26.

Consider the case in which $p=25\times10^{-4}$ mm. mercury. Expressing the pressure in hundredths of a millimetre we get :—

$$H=2{\cdot}7\times10^{-5}\times0{\cdot}25\ (292-91)\times1{,}725$$
$$=2{\cdot}34 \text{ calories per second}$$

and $M=\frac{H}{51}=0{\cdot}046$ grams per second (taking the latent heat as 51 calories per gram.).

This corresponds to an evaporation rate of 1·98 litres per minute.

Hence $G=1{\cdot}98\ L/M$

Also $L_p=L_0+G$

$$=(R+N)+G$$
$$=0{\cdot}275+1{\cdot}98 \text{ litres per minute (assuming } N \text{ constant)}$$
$$=2{\cdot}25 \text{ litres per minute.}$$

The observed value was 2·16 litres per minute which is less than the calculated by 0·09 litres per minute. When allowance is made for a small fall in N when the rate of delivery was increased this difference is reduced ; and the agreement between the observed and calculated values is thus fairly good.

Experiments on a 3-litre vessel with a silica adsorbent and a 1-litre vessel with charcoal gave similar results, although the agreement was not quite so close.

In all three cases the straight line law ceased to hold when the pressure rose to some value just below 0·01 mm., the limits appearing to be about 0·005 mm. and 0·008 mm. These correspond to mean free paths of about 10·2 and 6·4 mm., at the mean temperature of the evacuated space ; and as the distance between the envelopes was about 8 or 9 mm. the results accord with well-known laws.

At pressures somewhat above 0·01 mm. the slope of the graphs had fallen and there was marked flattening in the later stages when the M.F.P. was considerably reduced and the conductivity of the gas was more nearly constant.

TABLE I.

Rate of Evaporation in Litres per Minute ...	0·3	1·45	1·9	3·65	3·95	6·75	7·6	7·8	19·3
Pressure in mm. $\times10^{-4}$	0	0·2	0·4	0·8	1·2	6·2	13·75	18·8	Atmos. Pressure.

When the evacuated space was opened to the atmosphere the rate of evaporation was high and all the outer surface of the vessel (if in air) became heavily coated with frost. In a short time this caused the rate of evaporation to fall, as shown in Table II which relates to the 1-litre vessel. Similar results were obtained with two 3-litre vessels, the rates immediately after opening the tap being 19·3 L/M and 22·9 L/M. In the latter case the rate 43 minutes later was 16·9 L/M.

TABLE II.

Rate of Evaporation in Litres per Minute	0·35	0·35	9·55	9·7	9·3	8·25	6·5
Time in Minutes	0	10	10	13	15	25	45
		Opened to Atmosphere.					

In later experiments it was found that the neck losses fell rather rapidly at first as the gas flow increased, but that the rate of fall soon diminished (Table IX.). The pressure/delivery graph should show, therefore, a slight upward concavity in its initial stages. In certain cases this is discernible, but the high percentage error of the McLeod gauge at low pressures makes it difficult to find the shape of the curve at points not far from the origin.

When the graph has once been found for any vessel the observed rate of evaporation gives a sensitive indication of the pressure. Advantage of this may be taken when several vessels are connected in parallel, or when one only is used for testing adsorbents.

(B) *Relationship between the rate of evaporation of the cold liquid and the equilibrium pressure reached during evacuation.*

In the experiments considered the adsorbent was activated fruitstone charcoal. Preliminary experiments in an evacuated glass vessel showed that, over a moderate range, there was a nearly constant ratio between the equilibrium pressure, P, when the charcoal was heated, and that, p, reached when it was cooled by liquid oxygen. P/p was found to depend upon the proportion which the mass of the charcoal bore to the volume of the space. Thus, if the vessel held 1 gramme of the charcoal per 10 c.c. of evacuated space P/p was 40,000 : 1. In the 5-litre vessel itself there was only about 1 gramme per 470 c.c. of space, but P/p was 20,000 : 1. Lower values of P/p were found in a few cases when p was increased, the ratio not being quite constant when the range of pressure variation was too wide. In one vessel examined there was about 1 gramme of charcoal per 221 c.c. of space, but P/p was only about 6,000 : 1, although p was low. It is probable that charcoal of inferior activity had been inserted in this case. *See* (F) (1).

As the main aim of the experiments was to determine the losses of the vessels, a full investigation on adsorbents was not undertaken. It is of interest to note, however, that the values of P/p (now known as the Pressure Reduction factor) obtained are of about the same order as those found subsequently in an investigation by Lambert.[*] The magnitude of P/p was found by him to depend upon a number of factors, and no simple law of its variation was discovered.

It must be remembered that when the adsorbent is in a metal envelope gases evolved or adsorbed by the metal itself introduce complicatians. Also the adsorbent power of charcoals and of activated silica varies considerably.

Taking $P/p=20{,}000$ for the 5-litre vessel considered and substituting for p in equation (2) we get :—

$$L_p=0{\cdot}275+0{\cdot}0383\,P \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

where P is expressed in mm. of mercury.

(C) *Characteristic equations for standard vessels with charcoal adsorbents.*

Equations (2) and (5) hold for the particular 5-litre vessel tested and may be regarded as two of its *characteristic equations.*

---

[*] Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 81/86.

In the case of five other 5-litre vessels tested in 1919 the following mean values were obtained :—

$L_0 = 0{\cdot}24\ L/M$
$K = 0{\cdot}079$
$P/p = 31{,}000$ (when both expressed in the same units).

Hence the characteristic equations of vessels of this type are :—

$L_p = 0{\cdot}24 + 0{\cdot}079\ p$ . . . . (6) (p in mm. $\times 10^{-4}$)
$L_p = 0{\cdot}24 + 0{\cdot}0255\ P$ . . . . (7) (P in mm.)

These vessels were all of the same type as the first, and the higher value of P/p is due to the fact that more charcoal was used.

Relationships of the same kind were obtained with 25 and 1 litre vessels. When the characteristic equations for a given type of vessel have been determined, it is evident that they may be used for calculating :—

(1) The equilibrium pressure which must be reached during evacuation to secure a given rate of evaporation ; or the rate of evaporation if the vessel has been sealed when the equilibrium pressure has reached a measured value.

(2) The pressure of the residual gases :—

(*a*) When the vessel contains the liquid.

(*b*) When it is empty and has reached atmospheric temperature : or

the rate of evaporation when the pressure has risen to some measured value after a long period—say a year.

Since in the experiments the amounts of gas injected were measured, the *effective* activity of the adsorbent under the special conditions which exist in a metal vessel has been found.

(D) *Replacement of Charcoal by Activated Silica or Alumina.*

The use of silica in vacuum vessels appears to have been first suggested by Professor Dewar, and data relating to the adsorptive power of silica gel and other substances at atmospheric pressure were published by Dr. Briggs in March, 1921.*

At that time no experimental data relating to the activity of silica at very low pressures, nor to its use in a metal flask, were available in the Air Ministry Laboratory. Somewhat later in 1921 the author made some tests with silica gel, alumina, and aluminium hydroxide, and prepared four metal flasks for long-period tests under working conditions. One contained no adsorbent, one alumina, and the others different charges of silica gel. (For details of periodic tests *see* D.S.I.R. Report, §§ 240 to 250.) It was found that at atmospheric pressure, and also at very low pressures, silica was a better adsorbent than alumina, but was inferior to charcoal.

Thus in one case silica gel was heated to about 130° C. for a long period, and when 1 c.c. was used per 163 c.c. of evacuated space, the values of P and of p were 0·17 mm. (mercury) and $0{\cdot}83 \times 10^{-4}$ mm. respectively. Hence $P/p = 2{,}000$ approximately.

A rough calculation based on the assumption that the pressure-reducing factor is inversely proportional to the volume of the space evacuated gives a result of about the same order as that obtained by Lambert.* In the absence of an accurate knowledge of the law of variation, a closer comparison is hardly possible.

---

* "The Adsorption of Gas by Charcoal, Silica, and other Substances," Proc. Roy. Soc., A, Vol. 100 (1921).

In another experiment precipitated silica was heated very strongly, and this reduced its activity at atmospheric pressure. When used in a 3-litre vessel as in the other case, the factor obtained at first was about 200. As it was thought that moisture had been introduced accidentally during the injection of air, the apparatus was dried carefully and the experiment repeated. The factor then was about 900. There is little doubt that the lowness of this figure was due to partial deactivation produced by the strong preliminary heating.

In all the experiments the inner envelopes and the silica, which was placed in an internal capsule, were heated to 100° C. only during evacuation, and the factors obtained are those which correspond to these conditions. Copper itself appears to act as an adsorbent, and the factors are perhaps not strictly comparable with those found for adsorbents placed in glass vessels only and heated strongly during evacuation. (In the following cases the adsorbent was in its normal position in an internal capsule.)

(E) *Rate of Improvement of the Vacuum.*

(1) The pressure of the gas in the evacuated space of a Dewar vessel rises at once when air is admitted, and so does the rate of evaporation. These rises are both followed by a fall, which is rapid at first, and then slows down gradually, as a new state of equilibrium is approached. The effect of two successive injections of dry air in the case of a 5-litre vessel tested in October, 1919, is shown in Fig. 4. The first (20 c.c. at N.T.P.) caused the rate to rise suddenly from 0·365 *L/M* to 4·73 *L/M*, the rate ultimately obtained (18 hours later) being 0·75 *L/M*. The second (10 c.c.) produced a sudden rise from 0·77 *L/M* to 4·76 *L/M*, the final rate (19 hours after second injection) being 1·02 *L/M*.

The variations of the gauge reading are shown also, but while the rate of evaporation is varying the neck losses are not constant and the change in pressure does not give a measure of the change in the total rate of loss. Another complication is due to the fact that just after injections the pressures may be so high that they are no longer proportional to the gas conductivity. Further, unless the gauge is connected to the vessel by a short wide tube, its readings at any instant will not necessarily give the pressure in the vessel at that instant.

(2) Subsequent experiments made with vessels containing activated silica gave similar results, but much smaller injections were required.

Thus, in the case of one 3-litre vessel, 5 grammes of commercial precipitated silica was used, and two injections of dry air, each of about 0·5 c.c. (N.T.P.) were made. Equilibrium was approached more quickly than in case (*a*) Fig. 5.

(3) The effect of putting liquid oxygen into an evacuated 3-litre vessel containing silica is shown in Table III. Such a case is important because it illustrates the normal

TABLE III.

Evaporation Rate in *L/M*	1·07	0·81	0·696	0·629	0·592	0·555	—	—	0·545	0·526
Minutes	5	10	15	20	25	30	35	45	48	60
Pressure in mm. × 10^{-4} ...	16·5	12·5	8·87	7·33	5·93	—	4·69	4·69	—	4·69

NOTE.—Minimum Rate was 0·33 *L/M*.

---

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 81/86.

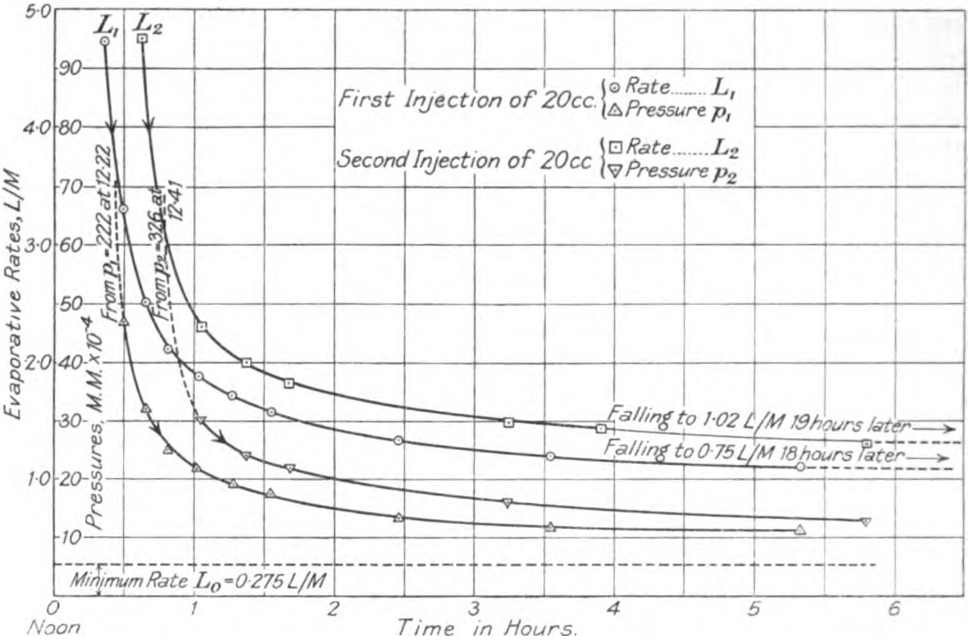


Fig. 4.—5 Litre Container with Charcoal Adsorbent. Effect, on Rate and Pressure, of Admitting Air.

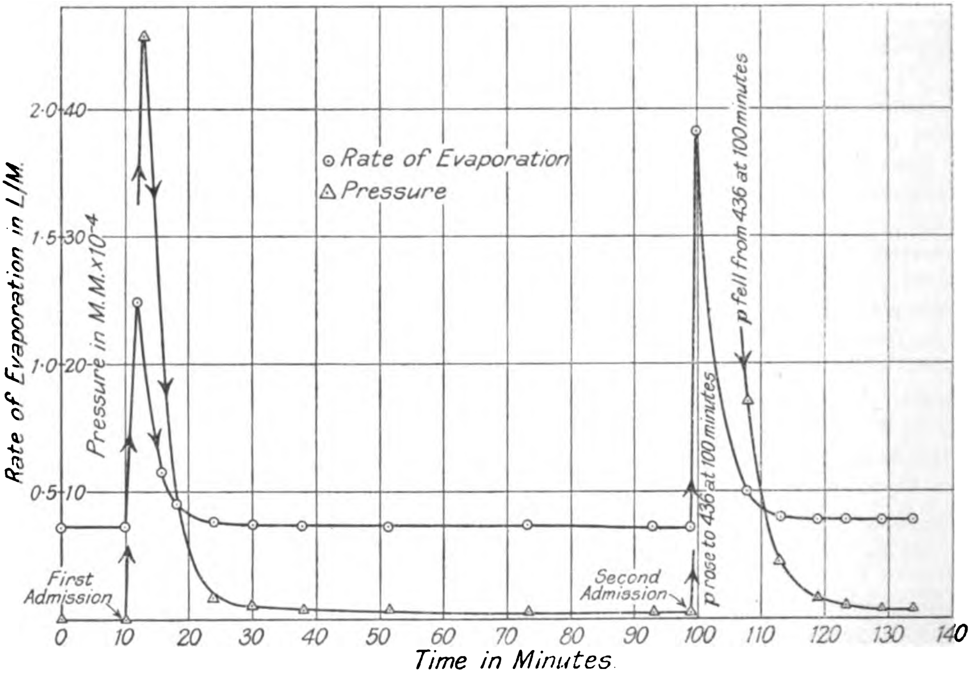


Fig. 5.—3 Litre Container with Silica Adsorbent. Effect, on Rate and Pressure, of Admitting Dry Air.

At time, 10 minutes 0·48 c.c. admitted.

„ 99 „ 0·52 c.c. „

effects in a sealed vessel which has just been filled. As the inner envelope has to be cooled down, there is a very heavy initial delivery of cold vapour, and at first the inner neck is cooled strongly. Wetting of the neck may occur while filling is going on, and at first the neck losses are very small. Some time must elapse, therefore, before the neck recovers and the conditions get steady.

(4) The changes of rate just after a permanently sealed vessel has been filled are shown in Table IV, two cases having been taken. One case of special interest is that of a 5-litre vessel with no adsorbent.

TABLE IV.

Evaporative Rate in L/M.	Minutes after Filling completed.	Total Delivery in Litres.	Minutes after Filling completed.
	First	*Vessel.*	
9·7	·0	0	0
8·26	·7		
6·85	2·1	21·2	2·7
6·04	2·7		
4·93	3·9	33·3	5·1
4·07	5·1		
3·72	5·7	39·7	6·9
3·32	6·2		
2·99	6·9	44·4	8·7
2·64	7·7		
2·30	8·7	51·0	12·2
2·04	9·7		
1·76	10·8	55·8	15·8
1·50	12·2		
1·29	13·9	60·3	20·2
1·14	15·8		
1·02	17·8	99·8	66·5
·923	20·2		
·872	22·7		
·835	25·3		
·810	28·0		
·806	30·9		
·795	33·7		
·795	36·7		
·793	39·5		
·785	42·6		
·789	45·5		
·788	48·5		
·787	51·5		
·787	54·5		
·789	57·5		
·781	60·4		
·781	66·5		
	Second	*Vessel.*	
5·7	0	0	0
3·31	2	5·7	2
1·44	3	8·08	3
0·64	5	10·16	5
0·46	15	15·66	15
0·413	30	22·15	30
0·408	40·5	26·46	40·5
0·406	50	30·36	50
0·406	57	34·06	57

Curves of this type, taken over a period of one hour after filling, give useful information regarding the state of a vessel and the activity of the adsorbent. The total loss during the "settling-down" period may be found by a counter on the spindle of the meter, or by plotting the time/rate curve, and integrating. Measurement by loss of weight over so short a period is not accurate.

(F) *Rise in the Rate of Evaporation.*

(1) In 1919 some new 5-litre vessels were tested soon after evacuation, and the rates of evaporation measured. Six months or more afterwards these had risen so much that a second evacuation was necessary. This was carried out, but although there was a considerable reduction, the initial values were not reached. Hence the rise in rate could not have been due entirely to deterioration of the vacuum, and the vessels were therefore opened. The polished surfaces were found to be coated with an almost invisible layer of dust and oil. This was merely wiped off, and the vessels were at once put together again and evacuated. As shown in the annexed table, the rates were then as low, or lower, than they were initially :—

TABLE V.

Vessel No.	" Evaporative Rate " (*L/M*).			
	Initial.	At End of Period.	After Second Evacuation.	Third Evacuation after Cleaning.
1	0·27	0·47	0·36	0·26
2	0·24	1·65	0·30	0·24
3	0·26	0·80	0·41	0·24
4	0·24	0·60	0·36	—
5	0·33	0·56	0·36	0·24

It was found that the admission of 20 c.c. of air to No. 3 changed the rate from 0·41 to 1·83 *L/M*. When the same amount of air was admitted to No. 5 the rate changed from 0·36 to 0·65 *L/M*. These differences were due to variations in the adsorptive powers of the charcoal. When measured they were all found to be very low, but that from No. 5 was much better than the other.

(2) By evacuation at 100° C. the "rate" of a new 3-litre vessel examined in 1920 was reduced from 1·44 *L/M* to 0·62 *L/M*. The inner surfaces were found to be coated with polishing powder and charcoal dust. "Pockets" of the powder left after buffing had not been removed, and dust had come out of the charcoal, which was held in position by coarse gauze. After the surfaces had been buffed and a dust filter fitted, the minimum rate was 0·39 *L/M*.

(3) About two years after a 1-litre vessel had been evacuated the rate was 0·67 *L/M* (one hour after filling). After a second evacuation the minimum rate was about 0·38 *L/M*. Dry air was then admitted until the rate was 0·65 *L/M*. The pressure was then about 12×10^{-4} mm. mercury. Assuming that after the two-year period the residual gases were air, the pressure of those gases when the vessel was in use was just over 12×10^{-4} mm. mercury—that is, it was of the order of 1/1,000 mm.

IV. SEPARATION OF RADIATION AND NECK LOSSES. EMISSIVITY.

The separate evaluation of R and in N equation (4) is rather difficult, because the neck losses are not due to simple conduction only. Heat can reach the liquid via the neck in several ways, viz. :—

(*a* By conduction down the metal of the inner neck.
(*b*) By gas conduction between the inner and outer necks.
(*c*) By radiation.
(*d*) By direct conduction and convection from the atmosphere to the liquid via the column of vapour.

Of these (*a*) is the most important ; and if the neck is long and narrow (*d*) is probably negligible. If the vessel is well evacuated (*b*) is very small. These variables are not all independent, and there is a complication due to abstraction of heat from the inner neck by the cold vapour. In consequence of this the neck losses are a function of the rate of gaseous delivery. It is possible to calculate them if certain assumptions are made,* but experimental determinations only are dealt with here.

Method 1.—*Effect of varying the sectional area of the neck metal.*

This method is described in Papers byBanneitz, Rhein and Kurze† and Briggs.‡

The rate of evaporation having been observed, a long, closely-fitting tube of the same material as the inner neck is pushed into that neck, forming a lining to the whole of its inner surface. The rate of evaporation finally attained is noted, and the neck losses deduced by a simple calculation.

Unfortunately, the conditions are not simple. Insertion of the liner not only changes the effective area of the neck, but alters its thermal state also, because of the increased flow of cold vapour. The calculation does not take this change of the conditions into account and can hardly give an accurate result. What the method actually gives is the rate of evaporation which will be obtained if the neck is replaced by one made of thicker metal.

Method 2.—*Effect of Shortening the Neck.*

It is important to find what increase will occur in the rate of evaporation if the neck of a given vessel is reduced in length. Comparisons made between vessels with long and with short necks are not of much value unless care is taken to secure equality in the radiation losses (a matter of some difficulty), especially in large vessels with slender necks. Further, samples of nickel-silver or cupro-nickel vary considerably in hardness and in electrical and thermal conductivity, and for this reason it is preferable to cut both inner necks from one piece of uniform tubing. If practicable, both bessels should be placed in one water bath with the evacuated spaces connected by a pipe.

The author prefers to use one vessel only, and to vary the effective length of its neck in one of two ways :—

(*a*) A long thick copper tube or sleeve, which fits the inner neck, is pushed a certain distance into it, thereby producing a thermal short-circuit of the part which it touches, and reducing the effective length by a known amount. To secure good contact the sleeve is first ground into the neck tube, and then split longitudinally in several places. (In one series of experiments, the thermal conductance of the sleeve per linear centimetre was about 40 times that of the neck tube, and the fit was such that it was difficult to remove the sleeve.)

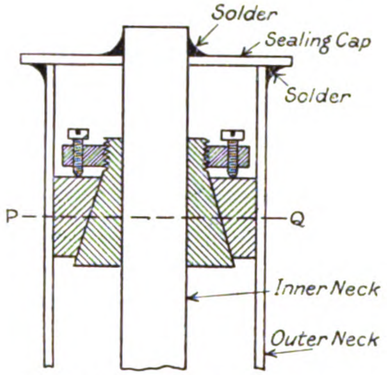
---

* Hogg, "A Note on the Conduction of Heat down the Necks of Metal Vacuum Vessels containing Liquid Oxygen," Trans. Faraday Society, No. 59, Vol. 20, Pt. 2, Nov. (1924)

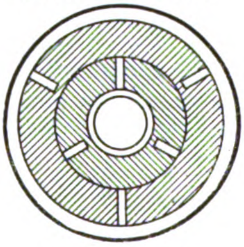
† "Investigations with regard to the principles of Construction of Containers for the transport of Liquid Gases," (translation) Annalen der Physik, 4th Series, Vol. 61 (1920).

‡ "An Experimental Analysis of the Losses by Evaporation of Liquid Air contained in Vacuum Flasks," Proc. Roy. Soc. Edinburgh, Vol. 41, Pt. 2, No. 10 (1921)

(*b*) The inner and outer necks are connected thermally by a short brass sleeve, which can be moved up or down, and clamped in any position (Fig. 6). The sleeve consists of male and female coned elements, which are split longitudinally, and may be pulled together by set screws. The tops of the necks are sealed together by a soldered metal washer, and when this is removed the screws may be turned. When the rotation is such that the male component is pulled into the female, the latter expands, and its outer cylindrical surface grips the inside of the outer tube. At the same time the male component is compressed, and its cylindrical inner surface grips the inner neck. The effective length may thus be varied without opening the body of the vessel and altering the constants appreciably.



Sectional Elevation.



Section on PQ

FIG. 6.—METHOD OF VARYING THE EFFECTIVE LENGTH OF THE NECK.

The relation between the effective length of the neck and the rate of evaporation in the case of a 3-litre vessel is shown in Table VI., the actual length of the inner neck being 20 cms. As might be expected, the graph flattens towards the right, and tends to approach a definite limit. Since an indefinite lengthening of the inner neck would decrease its conductance, but would not stop entry of heat by radiation and gaseous conduction, this limit does not give quite an accurate measure of the heat which enters by the body only.

TABLE VI.

Rate of evaporation in L/M ...	0·72	0·53	0·43	0·38	0·325	0·3[*]
Effective length of neck in cm. ...	3	5	8	10	15	20

Halving the effective length of the neck raised the total losses from 0·302 to 0·382 L/M, and the neck losses from 0·08 to 0·16 L/M—*i.e.*, from 26 to 42 per cent.

Hogg,[†] from theoretical considerations applied to a 3-litre vessel with a neck 16·5 cms. long, concluded that the normal loss of 0·3 L/M would be raised in the corresponding case to 0·4 L/M, and that the neck losses would be 19 and 40 per cent.

Table VII. gives the relationship for a 25-litre container with a neck 30·5 cms. long, the vacuum being rather poor. Halving the effective length of the neck raised the total losses from 0·716 to 0·79 L/M, and the neck losses from about 0·006 L/M to 0·08 L/M, corresponding to about 1 and 10 per cent. Hogg's calculation for such a vessel when well evacuated gives total losses of 0·5 and 0·56, and neck losses of 0·02 and 0·08—*i.e.*, 2 and 13 per cent. respectively.

TABLE VII.

Rate of evaporation in L/M ...	0·86	0·79	0·745	0·736	0·726	0·716
Effective length of inner neck in cm.	10·2	15·2	20·3	22·9	25·4	30·5

Method 3.—*Measurement of Neck Losses by Cooling the Neck.*

The charged vessel is placed in a bath and the "rate" noted. A cup which surrounds the upper part of the neck is then filled with liquid oxygen, and is replenished until the rate is again steady. Little or no heat can then pass down the inner neck by conduction, and the difference between the two observed rates gives an approximate measure of the neck losses. As it is difficult to cool the whole of the outer neck without cooling the body, the passage of heat into the inner neck by radiation and gas conduction cannot be stopped entirely. This transfer is not very great, however, and it is thought that the results obtained are not without value. Care must be taken to keep the temperature of the body of the vessel as constant as possible.

In the following examples the necks of all the vessels were nominally alike:—

(*a*) The evaporative rate of a 1-litre vessel fell gradually from 0·57 L/M to 0·336 L/M, giving a neck loss of 0·234 L/M.

Values of 0·232 and 0·221 were found in later experiments.

(*b*) Similar experiments with a 3-litre vessel gave the following results:—

TABLE VIII.

Date.	Initial rate.	Final rate.	Difference.
22/12/22	0·31	0·24	0·07
27/3/23	0·322	0·248	0·074

---

[*] Tends to approach a lower limit.

[†] "A Note on the Conduction of Heat down the Necks of Metal Vacuum Vessels containing Liquid Oxygen," Trans. Faraday Society, No. 59, Vol. 20, Pt. 2, November (1924).

(*c*) A 5-litre vessel with no adsorbent was evacuated in July, 1921, and its rate was found to be rising gradually on account of the steady rise in the pressure of the residual gases.

On 6/1/23, the initial and final rates were 0·77 L/M and 0·74 L/M, giving a neck loss of 0·03 L/M.

The low value of the neck losses in (*c*) is almost certainly due to the cooling action of the heavy flow of vapour, the additional effect of the liquid in the cup not being very great.

As the high value of both neck losses and rates of evaporation in (*a*) seemed anomalous the vessel was opened. The electrical resistance of the inner neck was abnormally low, and the thermal conductance was higher than usual. The high rates of evaporation were due partly to defective polish and partly to poor vacuum. Also, as the shells were cylindrical, with rounded ends, the ratio of surface to volume was rather high.

Method 4.—*Neck and Radiation Losses, Emissivity.*

As the amount of heat transferred by radiation between two polished surfaces which differ in temperature depends upon the emissivities and as these may vary with the wavelength, there will be some uncertainty if the law of variation is not known. In calculations relating to the Dewar vessel it is therefore desirable to use data obtained by experiment on an actual vacuum vessel, in order to ensure similarity of conditions.

It can be shown* that the amount of heat transferred by radiation in a Dewar vessel is approximately equal to—

$$A \times \frac{E}{2} \times 10^{-2} \text{ calories per second,}$$

where A is the area of the inner shell in square centimetres, and E the emissivity of the inner surface of the outer shell at some definite temperature, say, 20°C. (The emissivity of a " black body " is taken as unity.) Hence, if the latent heat of liquid oxygen is 51 calories per gram, the rate of evaporation R, due to radiation only, will be

$$\begin{aligned} R &= A \times E \times 0{\cdot}35 \text{ grams per hour,} \\ &= A \times E \times 0{\cdot}00423 \text{ litres of gas per minute (N.T.P.).} \end{aligned}$$

(since 1 gram per hour corresponds to 0·012 litre of gas per minute).

Hence,
$$E = 236 \times \frac{R}{A} \qquad \text{(8)}$$

(R being in litres per minute).

In a well-evacuated vessel the only losses of any importance are the radiation and neck losses.

$$\therefore\ E = 236 \frac{L_0 - N}{A}, \qquad \text{(9)}$$

where L_0 is the observed rate of evaporation.

In determining E by this method the vessel should have a large body and a long slender inner neck of thin material. L_0 will then be large, and the flow of vapour will make N small. Serious errors may be made if a small vessel with a short neck is used, or if the vessel is of a badly conducting material such as glass, and is only partially full.

---

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, paragraphs 29/37.

Samples of glass differ widely in physical characteristics, and variations of temperature lead to changes in the conductance.

If the body of the vessel is made of a bad conductor there may be an appreciable temperature gradient between the base of the inner neck and the surface of the liquid. This may lead to complications, and render a reasonably accurate determination difficult or impossible.

Examples.

(*a*) *Obtaining E and R.*—After a prolonged evacuation a 25-litre container was losing vapour at the rate of 0·44 litre per minute, $A=3970$.

$$\therefore \quad E=0{\cdot}0595\ (0{\cdot}44-N).$$

From preliminary experiments it was concluded that N was not greater than 0·04 L/M nor less than 0·02 L/M, giving for E the values 0·0238 and 0·0262, with a probable value of about 0·0244.

This gives the radiation loss $R=0{\cdot}41\ L/M$.

The value given for the emissivity of copper by Hagen and Rubens* is 0·16; but, apart from possible variations in the nature of the radiation, constants obtained for pure metals are not necessarily applicable to commercial ones, which have been spun, pressed or partially annealed. The polish reached during manufacture is not so high as that obtainable with a small area which is not part of an actual vacuum vessel; and the emissivity may be affected by the removal of adsorbed gases during evacuation.

(*b*) *Finding N and R.*—The values of E or of R obtained by experiments on a large vessel may be used for finding the losses on a smaller vessel, in which N is not small in comparison with R or L_0.

Thus in one 3-litre vessel tested

$$L_0=0{\cdot}222\ L/M, \quad A=1{,}142 \text{ sq. cm.}$$

$$N=L_0-\frac{EA}{236}=0{\cdot}104\ L/M \text{ and } R=0{\cdot}118\ L/M.$$

Method 5.—*Change in the Neck Losses Due to a Variation in the Rate of Gas Flow.*

The rate of evaporation L_0 is raised to some steady value L_1 by sending a current through a coil immersed in the liquid oxygen and the input in watts noted. The current is then increased until the rate of evaporation becomes steady at another value L_2, and the watts are again measured.

Let N_0, N_1 and N_2 = neck losses at deliveries L_0, L_1 and L_2.
,, W_1 and W_2 = losses due to the watts.
,, w = the losses due to the leads.
,, R = losses due to body radiation.

---

* Report of the Oxygen Research Committee, Department of Scientific and Industrial Research, 1923, Paragraph 37, Table 4.

Then, if the vacuum is high, gas conduction is negligible, and we have

$$L_0=R+N_0 \qquad (10)$$

$$L_1=R+N_1+W_1+w \qquad (11)$$

$$L_2=R+N_2+W_2+w \qquad (12)$$

Hence the change in the neck losses is

$$N_1-N_2=(W_2-W_1)-(L_2-L_1) \qquad (13)$$

W_1 and W_2 may be calculated from the latent heat of liquid oxygen or found by experiment.

If it is assumed that when the gas flow becomes L_m the cold vapour abstracts all the heat flowing down the inner neck, the corresponding neck loss becomes zero.

Hence, from equation (13)

$$N_1=(W_m-W_1)-(L_m-L_1) \qquad (14)$$

where W_m is the loss due to the heater when the delivery is L_m.

The radiation losses may then be calculated, and also the neck loss corresponding to any given flow.

Method 6.—*Two-Vessel Method.*

Instead of making the assumption just mentioned, an experiment is made with a supplementary vessel, and the unknowns can then be eliminated. Both vessels must be of the same materials and the necks must be exactly alike, but the bodies must be of different sizes. Also, a high vacuum must be maintained in the vessels throughout the experiment.

The delivery of the smaller vessel is brought up to that of the larger by the heater, and the input of watts noted. The current is then cut off, and the gas flow measured immediately by a well-damped reflecting flow-meter.

Let L=normal rate of evaporation for large vessel.
,, N=neck loss at delivery L.
,, R and r=radiation loss of large and small vessels (bodies only).
,, A and a=area of inner shell of large and small vessels (bodies only).
,, W=loss due to watts.
,, w=loss due to leads.
,, l_0=rate of evaporation for small vessel just after current is cut off.

Then, since gas conductance is negligible

$$L=R+N \text{ (large vessel)} \qquad (15)$$

Now the neck losses of both vessels are equal, because the deliveries are the same. Hence

$$L=r+N+W+w \text{ (small vessel)} \qquad (16)$$

$$=R\left(\frac{a}{A}\right)+N+(W+w) \qquad (17)$$

Eliminating, we get

$$N=L-(W+w)\left(\frac{A}{A-a}\right) \qquad (18)$$

$$R=(W+w)\left(\frac{A}{A-a}\right) \qquad (19)$$

$$r=(W+w)\left(\frac{a}{A-a}\right) \qquad (20)$$

Also, for a moment after the current has been cut off, the neck of the small vessel remains in the thermal state which corresponds to a delivery L and neck loss N.

Hence
$$l_0=r+N+w \qquad (21)$$

∴ from equation (18)

$$N=(l_0-w)\left(\frac{A}{A-a}\right)-L\left(\frac{a}{A-a}\right) \qquad (22)$$

W may be found as before; and w by measuring, by a reflecting flow meter, the small rise produced in the rate of evaporation when the coil, with no current flowing in it, is put into the liquid. The slight increase in the flow of cold vapour will have very little effect on N, but before the coil is immersed it should be cooled in liquid oxygen.

The loss w may be reduced by using one lead only, and completing the circuit by the inner vessel and neck.

Since N is usually small, and in equation (18) is given as a difference between two terms, a small error in measuring either may lead to a considerable percentage error in the result. For this reason it is preferable in some cases to find W by a separate experiment, the same heating coil being used. The latent heat need then not be known, and if the same meter is used for measuring both L and W the error in N will be reduced.

Equation (18) may be written

$$N=L-\frac{(W+w)}{1-\frac{r}{R}} \qquad (23)$$

If the inner surfaces of the vessels are not polished equally well, or if the external temperatures differ slightly, $\frac{r}{R}$ will not be equal to $\frac{a}{A}$. The error may be reduced by making $\frac{r}{R}$ small. One vessel therefore should be much smaller than the other.

In experiments on radiation losses w may be eliminated by passing the current through compensating leads attached to a duplicate or dummy coil in the larger vessel. The leads are short-circuited near the bottom, and the coil has a break in it. w will then be the same for each vessel, and we get

$$\frac{R}{A}=\frac{W}{A-a}$$

which involves only W and the difference between the areas. Also, from equation (9)

$$E=236\,W\left(\frac{1}{A-a}\right) \qquad (24)$$

A somewhat different case is that of vessels which have equal necks of the same material but bodies of different materials. The heater is used to bring the lower delivery L_2 up to the higher L_1, and we find

$$R_1-R_2=W-(G_1-G_2) \qquad (25)$$

If G_1 and G_2 are negligible

$$R_1-R_2=W \qquad (26)$$

Thus, if the radiation loss of one vessel is known that of the other may be found, and the emissivities compared. The " cut-off " method may be applied here also. If the relative sizes of the bodies have been so adjusted that $L_1 = L_2$ no heater will be required. The neck losses will then be equal and $R_1 = R_2$.

Hence
$$\frac{E_1}{E_2} = \frac{A_2}{A_1} \quad \ldots\ldots\ldots\ldots\ldots \quad (27)$$

where the A's are the radiating areas.

If the bodies are equal and the evacuated spaces are in communication, then $G_1 = G_2$ and equation (26) still holds.

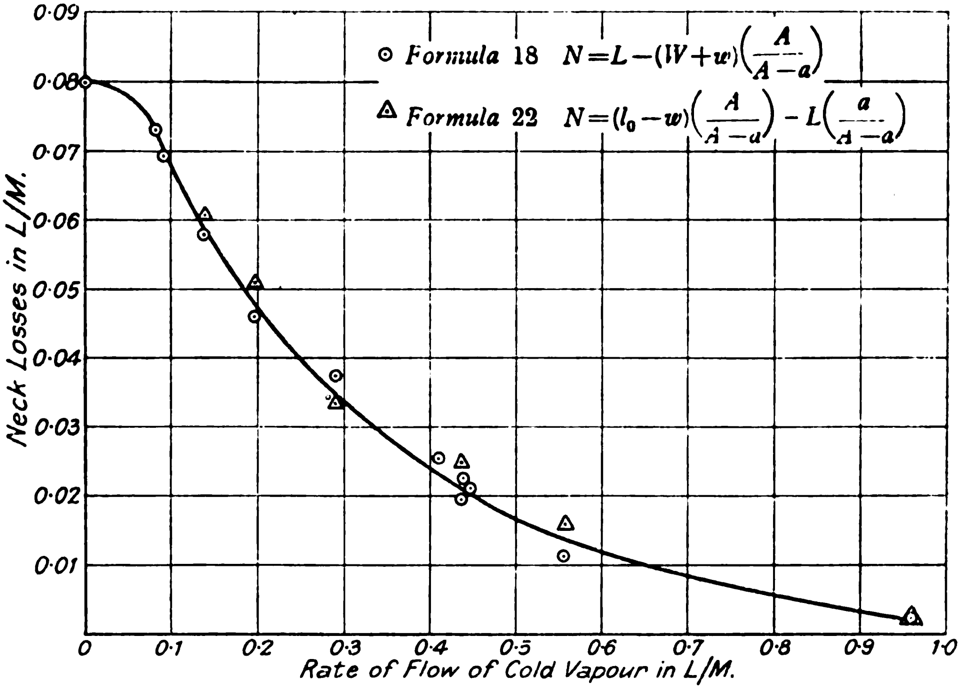


FIG. 7.—EFFECT OF FLOW OF COLD VAPOUR ON NECK LOSSES OF 25 LITRE CONTAINER. (Two-vessel Method).

Errors due to imperfect evacuation will therefore be eliminated, or at least reduced.

In all the following examples the same small supplementary vessel was used. The diameter of the inner shell was 5·3 cms.; and both shells were so designed that any standard inner or outer neck could be soldered to them.

(*a*) The neck losses of a 25 litre container at various rates of gas flow are shown in Fig. 7; and, as will be seen, they fell from 0·073 L/M to 0·004 L/M when the total delivery was increased from 0·082 L/M to 0·96 L/M.

Rather higher values were given by equation (22) (" cut-off " method).

A rough calculation based on the mean conductivity of the neck metal, and neglecting radiation into the neck, gave about 0·08 L/M as the probable value which

N would have if none of the evolved vapour passed through the neck, a condition which obviously cannot hold for an actual vessel. As the graph, however, shows the relationship between the amount of heat transmitted by a definite piece of neck tubing, and the flow L of cold vapour through it, quite irrespectively of how the flow has been produced, the flow of cold vapour may be supposed to be cut off or put equal to zero.

On plunging the body of the small vessel into liquid oxygen the immediate fall in the rate was 0·01 L/M, which gives r approximately. A greater fall took place later as the outer neck became progressively cooler by direct conduction of heat downwards.

(*b*) Other examples are shown in Tables IX to XI.

Table IX.—*Vaporizer Neck Tubing. Losses at Various Deliveries.*

Rate of flow in L/M.	Neck losses, N, in L/M *by method*			
	6 (Eqn. 18).	6 (Eqn. 22).	3.	4.
0·175	0·138	0·128	...	...
0·218	0·122	0·112	...	...
0·222	...	...	...	0·104
0·234	0·116	0·106	...	...
0·267	0·098	0·088	...	...
0·32	...	...	0·07	...
0·77	...	...	0·03	...

Had the vapour not cooled the neck value of N, by a rough calculation as in Method 6, paragraph (*a*), would have been about 0·16 to 0·2 L/M.

Table X.—*Radiation Losses of Various Vessels.*

Vessel.	Radiation Loss in L/M.	
	Method 6.	By cooling body.
25 litres	0·423	...
5 ,, ...	0·172	...
3 ,, ...	0·121	...
1 ,, ...	0·065	...
Supplementary	0·0097	0·01

Table XI.—*Radiation Loss of* 3 *Litre Vessel by Method* 6. *Emissivity.*

By experiment on small vessel and vessel of capacity.	Equation 18	∴ E.	Equation 22.	∴ E.
	R.		R.	
25 litres	0·121	0·0251	0·121	0·0251
5 ,, ...	0·119	0·0246	0·126	0·0260
3 ,, ...	0·118	0·0244	0·128	0·0265

Mean value of E =0·0253.
By method (4) R=0·118 L/M.
E=0·0265.

DISCUSSION.

Prof. O. W. Richardson said that as a rather heavy consumer of vacuum flasks he had often wondered how much heat is lost by conduction along the neck, and it was very satisfactory to know that such loss is inconsiderable.

Mr. G. R. D. **Hogg** said that the Oxygen Research Committee had been faced with the absence of any data for determining the relative importance of the various ways in which heat is lost from vacuum vessels, and the present research was undertaken at their instance. Some idea of the practical difficulties overcome by the author could be gathered from the fact that, in one flask, 7 ft. of soldered jointing had to be unmade and remade from time to time. He thought that the author's experiments, confirmed by some calculations for which he was himself responsible, had gone far towards providing satisfactory information for the use of designers of flasks.

Dr. G. W. C. **Kaye** said he understood that great difficulty is experienced in "outgassing" the adsorbent which is employed for the purpose of keeping up the vacuum, as the temperature cannot be raised very high without damaging the soft-soldered joints. Would not silver-soldering or brazing be a better method of jointing?

Author's reply (communicated): I have been aware for a long time that a metal surface cannot be out-gassed properly by heating to so low a temperature as 100°C. I have made a practice of heating the outer shells during evacuation by applying a flame cautiously; but this cannot, of course, be done to parts near the soft-soldered joints. Unfortunately, brazing or silver-soldering makes the metal too soft to stand reasonably rough usage, and it is difficult to see how serious tarnishing of the metal can be avoided during assembly. A special process would have to be developed; and this might be difficult and probably would be expensive. It must be remembered that the adsorbent is put into the vessel with the express object of making the initial evacuation easy and adsorbing gases which may diffuse gradually from the metal into the evacuated space. Vessels properly evacuated at 100°C. maintain low rates of evaporation for long periods, and re-evacuation is neither difficult nor costly. Some years ago the Germans experimented with welded vessels, but do not appear to have adopted the process commercially. Both German and French vessels now on the market are, I believe, made with soft-soldered joints. The reason is probably financial.

DEMONSTRATION OF THE APPLICATION OF THE PIEZO ELECTRIC PROPERTIES OF A ROCHELLE SALT CRYSTAL AND THE TRI-ELECTRODE VALVE TO THE DETERMINATION OF IMPACT STRESSES IN GRANULAR MATERIAL.

By J. J. HARTLEY, *M.Eng.*, *M.Sc.*, *A.M.I.C.E.*, and R. H. RINALDI.

THE distribution of stress in granular material under a continued load with the essential minimum of movement in the measuring apparatus has been determined by several observers, including Goldbeck (Proc. Am. Soc. for Test. Mat., 1917), Shaxby and Evans (Trans. Far. Soc., 1923); but the apparatus employed by these investigators does not appear to be adapted for the investigation of instantaneous loads.

For the purpose of the investigation of this problem the present instrument has been designed. The apparatus consists of a Rochelle salt crystal which is subjected to axial compression by means of three springs, this pressure remaining constant throughout the experiment. The variation in electric potential which is made use of is obtained by the application of torsion; for, as noted by Nicholson, the piezo-electric effects in the case of Rochelle salts are more pronounced when the crystal is subjected to torsion than are those obtained by axial loading.

One pole of the crystal—that is to say, the negative—is connected to the grid of a tri-electrode valve, and modifies the grid bias according to the amount of the torsion. The relation between these two factors is not a linear one, but gives when plotted the same type of curve as the ordinary valve characteristic, and the initial tension is so adjusted that with the actual torsion applied the slope of this applied torsion, grid potential curve is a maximum. In the same way the permanent grid bias is chosen so as to give a maximum slope to the anode current, grid potential curve.

The other pole of the crystal is earthed, and the effect is thus similar to that obtained when a charged ebonite rod fs applied to the grid.

The chief difficulty in the satisfactory calibration of the apparatus has been found to be the surface leakage of the crystal, which varies to a considerable extent with the atmospheric conditions.

Coating the crystal with varnish and paraffin wax has been tried, but up to the present with only moderate success.

The sensitivity of the electrical mechanism, when using a Marconi R type valve with 40 volts high tension and no permanent grid bias, is about 100 micro-ampere change in plate current per 100 grams increase in load under the best atmospheric conditions. This sensitivity could be easily increased if necessary by increase in the spring tensions, or by more complete drying of the crystal; but such increased sensitivity is only obtained at the expense of the mechanical strength.

DEMONSTRATION OF SOME SURFACE TENSION PHENOMENA

By Edwin Edser.

(*a*) It is well known that when a water surface is touched with an oily needle the small quantity of oil applied spreads rapidly, as may be shown by covering the surface with lycopodium powder. In the present instance it was shown that a hydrocarbon oil does not spread in this way if it be perfectly pure, whereas the slightest touch of a needle fouled with oleic acid produces an immediate effect.

(*b*) A quantity of pure paraffin oil was floated on water, the interface being shown in optical projection by means of a layer of freshly-prepared aluminium powder which rested on the water. A drop of oleic acid from a capillary tube was allowed to sink through the paraffin, and on reaching the interface it immediately spread with great rapidity, carrying the aluminium powder with it.

(*c*) It might be expected that a spot of pure paraffin floating on water would arrange itself so that its upper and lower surfaces meet at an acute angle, their line of inter-section with one another being coincident with their line of intersection with the water surface. It was shown by optical projection, however, that the edge of the spot is " tucked under," the water surface intersecting the lower surface of the spot along a line below the latter's maximum horizontal cross-section. Fouling of the water surface with a small quantity of oleic acid causes the paraffin to collect itself into rounded drops.

FURTHER DEMONSTRATION OF SURFACE TENSION PHENOMENA

By Prof. C. R. Darling.

THE experiments shown related to the Paper by R. S. Burdon on "The Spreading of One Liquid Over Another," read before the Society on December 11.

(*d*) The spreading of pure water over a clean mercury surface, illustrated in Figs. 3-5 of Burdon's Paper, was shown to be identical with that of olive oil on water. The beaded ridge at the edge and the holes in the internal portion are present in both cases. The water surface had a diameter of 9 cms., and the drop of oil measured about 0·05 c.c. It was further shown that the water surface beyond the main drop was covered with a thin layer of oil, and that a second drop placed outside the first did not expand. The original drop, after expanding, gradually shrank, and broke up into two or three portions, each of which assumed a permanent lenticular shape.

(*e*) The formation of holes in films after spreading was shown to be a common phenomenon, and was illustrated by placing drops of the following liquids on water surfaces: Quinoline, nitrobenzene and dimethylaniline, the after-results in each case being the partition of the film by canals spreading from hole to hole, ending in the production of numerous globules; and tar-oil, in which case the film heaped up round the holes, giving rise to a cellular formation.

(*f*) In order to illustrate a suggestion that the changes in the film after spreading are due to alterations in the interfacial tension, the result of changing this tension was shown in the case of a large globule of light lubricating oil floating on water. A drop of quinoline was allowed to fall on to the globule, through which it sank. On reaching the junction of the oil and water the quinoline altered the interfacial tension, when the oil globule was shattered with almost explosive violence.

The view was expressed that when a drop of one liquid is placed on the surface of another, a thin layer (possibly monomolecular) flashes across the surface, drawing out the main mass of the floating drop. The expanded drop, however, is in unstable equilibrium, and the interfacial tension gradually asserts itself and gradually restores the distorted drop to the lenticular shape, which is then stable, or gives rise to a number of smaller globules. The holes formed in the films are evidence of a state of strain existing between the boundary ridges.

It was mentioned that the ridge stated by Burdon as being first noticed by Osborne Reynolds was referred to by Prof. James Thomson in his Paper before the British Association in 1855, in which the phenomenon of "tears and wine" was first explained. Between the falling "tears" a ridge of liquid was observed to rise, forming the material for subsequent drops. This is similar to the rising ridge described by Burdon as occurring when water drains from a sheet of perfectly clean glass.

Physics

JUL 27 1926

THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 38.—PART 4.
JUNE 15, 1926.

Price to Non-Fellows **6s.** *net, post free* **6/3.**
Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:
FLEETWAY PRESS, LTD.,
3-9, DANE STREET, HIGH HOLBORN, W.C.1.

1926.

THE PHYSICAL SOCIETY OF LONDON

1926-27.

OFFICERS AND COUNCIL.

President

PROF. O. W. RICHARDSON, M.A., D.Sc., F.R.S.

Vice-Presidents

(WHO HAVE FILLED THE OFFICE OF PRESIDENT.)

PRINCIPAL SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, C.B.E., M.A., LL.D., F.R.S.
SIR A. SCHUSTER, PH.D., ScD., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. V. BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E, M.A., F.R.S.
ALEXANDER RUSSELL, M.A., D.Sc., F.R.S.
F. E. SMITH, C.B.E., F.R.S.

Vice-Presidents

PROF. F. LLOYD HOPWOOD, D.Sc.
D. OWEN, B.A., D.Sc.
E. H. RAYNER, M.A., Sc.D.
J. H. VINCENT, D.Sc., M.A.

Secretaries

PROF. A. O. RANKINE, O.B.E., D.Sc.
Imperial College of Science and Technology, S. Kensington, S.W.7.

J. GUILD, A.R.C.S., D.I.C., F.INST.P.
Lalbagh, Park Road, Teddington, Middlesex.

Foreign Secretary

SIR A. SCHUSTER, K.B.E., PH.D., Sc.D., F.R.S.

Treasurer

R. S. WHIPPLE
45, *Grosvenor Place,* S.W.1.

Librarian

J. H. BRINKWORTH, M.Sc., A.R.C.S.
Imperial College of Science and Technology, S. Kensington, S.W.7.

Other Members of Council

D. W. DYE, B.Sc.
A. FERGUSON, M.A., D.Sc.
E. A. OWEN, M.A., D.Sc.
SIR RICHARD PAGET, BART.
R. W. PAUL.
J. ROBINSON, M.Sc., PH.D.
J. S. G. THOMAS, D.Sc.
W. S. TUCKER, D.Sc.
PROF. A. M. TYNDALL, D.Sc.
A. B. WOOD, D.Sc.

Assistant Secretary (Publications)

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley,* N.3.

XXVIII.—OBLIQUITY CORRECTIONS IN RADIUM ESTIMATION.

By IVOR BACKHURST, *M.Sc.*, The National Physical Laboratory.

Received February 12, 1926.

ABSTRACT.

Formulæ are given for obliquity corrections in radium estimation applicable to sources of the shapes most frequently occurring in practice. The effect of scattered radiation is considered and some experimental results are shown graphically and compared with theory. Calculated values for a particular case are given by way of example.

WHEN the γ-ray method is used to determine the radium content of a tube having dimensions considerably larger than the radium standard with which comparison is to be made, it may be necessary to apply a correction to allow for the difference in distribution of the two sources. In the case of a long tube placed perpendicular to the axis of the ionization chamber, the parts of the source are at a greater average distance from the latter than in the case of a short tube placed in the same position, and, on account of greater average obliquity, the rays from the longer tube are absorbed to a somewhat larger extent in the lead front of the ionization chamber. The case arises, for example, in the determination of the radium content of a luminous compound. The amount of radium element normally contained in a tube 12 cms. long and 2 cms. diameter filled with compound constitutes a comparatively weak source, so that when 0·5 cm. of lead is used on the front of the ionization chamber, it becomes desirable to effect the determination with the radium distant not more than about 25 or 30 cms. from the latter. Under these conditions the correction for obliquity may amount to 2·5 per cent. A further correction should be applied to allow for absorption of the γ-rays in the compound itself.*

The obliquity correction may be complicated by the effect of scattered radiation if the radium bench is near a wall, or if a substantial stand is used as a holder for the radium.

POINT SOURCE.

The ionization produced by the direct action of the γ-rays on the air in the ionization chamber may be assumed to be small compared with that caused by the electronic radiation excited in the lead walls of the chamber or in metal parts inside it. If the chamber contains only a thin brass electrode, most of the ionization will be due to radiation from the lead walls.

If it is further assumed that the ionizing power of the electronic radiation from a particular area of metal surface inside the chamber is directly proportional to the intensity of the γ-radiation crossing that surface, but independent of the direction of the γ-radiation, then, since absorption of the γ-rays in the air inside the ionization chamber may be neglected, we have in the case of a point source, assuming to begin with that absorption in the lead walls of the chamber remains constant, that the ionization effect " E " is proportional to the solid angle " w " of the tangent cone drawn from the point source to the inner surface of the ionization chamber. In the case of a cylindrical ionization chamber of internal radius " a," the solid angle " w " is for any point distant from the axis of the chamber produced less than " a," the same as the angle subtended by the circular front of the ionization chamber at that point.

---

* "The Estimation of the Radium Content of Radioactive Luminous Compounds," by Owen and Fage, Proc. Phys. Soc., Vol. 34, I, pp. 27-32 (December, 1921).

The solid angle subtended by a circle at any point may be expressed with the aid of elliptic functions, or alternatively by means of zonal harmonics. The former method is normally not so convenient as the latter, as in most practical cases the zonal harmonic series converges sufficiently rapidly. If the radius of the circular front of the ionization chamber, denoted by " a " is 7·25 cms., and " d " the distance of the point P from the chamber measured along the axis is 25 cms., we have provided that " y " the distance of P from the axis is not greater than "a," that

$$w=2\pi\left\{\frac{1}{2}p^2 . P_1(c) -\frac{3}{8}p^4 . P_3(c)+\frac{5}{16}p^6 . P_5(c)\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

to an accuracy of about 1/10,000.

In the above expression $p=\frac{ac}{d}$, where $c=\cos\theta$, and $\tan\theta=\frac{y}{d}=T$.

$$P_1(c)=c.$$

$$P_3(c)=\tfrac{1}{2}(5c^3-3c)$$

$$P_5(c)=\tfrac{1}{8}(63c^5-70c^3+15c)$$

UNIFORM LINE SOURCE.

In order to find the effect of a line source cutting the axis perpendicularly, it is convenient to express (1) in terms of powers of tan θ or y. Writing (1) in powers of c, we have

$$w/2\pi=\frac{1}{2}k^2c^3+\frac{9}{16}k^4c^5+\left(-\frac{15}{16}k^4+\frac{75}{128}k^6\right)c^7-\frac{350}{128}k^6c^9+\frac{315}{128}k^6c^{11}$$

where $k=a/d$. Since T is not greater than 0·29, we may put $c=1-\frac{1}{2}T^2+\frac{3}{8}T^4$, with an error of less than 1/20,000. This gives

$$w/2\pi=\text{Vers}\ \varphi-LT^2+MT^4-NT^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $L=3K^2-30K^4+132K^6$

$M=3{\cdot}75K^2-80K^4$

$N=2{\cdot}5K^2$

and $K=k/2=a/2d$

and $\tan\varphi=k=a/d$

Terms smaller than k^2T^6 are omitted.

The last term of (2) will in most cases be negligible.

Assuming the ionization effect to be proportional to w, we have on integrating (2) with respect to "y," since $y=Td$, that

$$E \propto d\{\text{Vers}\,\varphi(T_2-T_1)-L(T_2^3-T_1^3)/3+M(T_2^5-T_1^5)/5-N(T_2^7-T_1^7)/7\}$$

where E is the effect produced by a uniform line source cutting the axis perpendicularly and extending from $y=y_1$ to $y=y_2$, so that $T_1=y_1/d$ and $T_2=y_2/d$.

In the case of a narrow tube "l" cms. long, bisected by the axis, the percentage correction to be applied to the measured value, in order to obtain the effect that would be produced by the same quantity of radium concentrated on the axis at the middle of the tube, will therefore be given by

$$\frac{100\{LT^2/3-MT^4/5+NT^6/7\}}{\text{Vers}\,\varphi-\{LT^2/3-MT^4/5+NT^6/7\}} \quad \dots\dots\dots\dots \quad (3)$$

where $T=l/2d$.

FORMULÆ ALLOWING FOR THE CHANGE IN ABSORPTION IN THE LEAD FRONT OF THE IONIZATION CHAMBER DUE TO OBLIQUITY.

If the radium is not brought nearer than about 25 cms. to an ionization chamber of diameter about 14 cms., and is nowhere more than 7 cms. from the axis, an expression for the ionization effect may be found that is sufficiently accurate for most purposes, and that takes into account the change in absorption in the lead front of the ionization chamber due to obliquity.

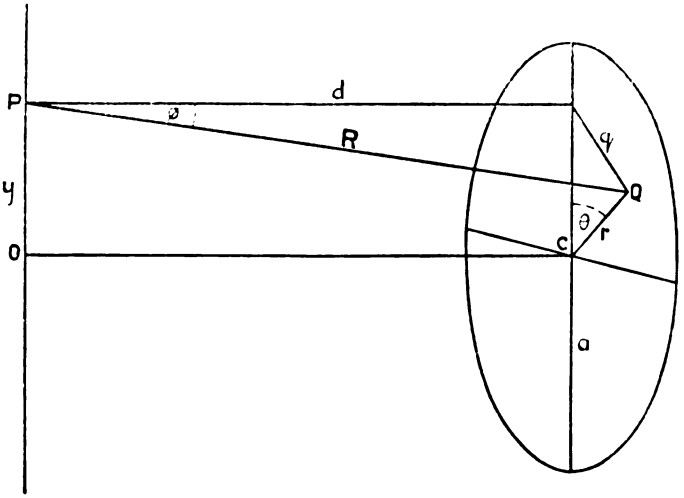


FIG. 1.

POINT SOURCE.

In Fig. 1 let PQ represent a ray from a source at P cutting the inner surface of the front of the ionization chamber at Q, the axis of the chamber lying along OC. Then from the figure

$$R^2=d^2+q^2=d^2+r^2-2ry\cos\theta+y^2$$

If μ is the absorption coefficient in the lead front of thickness t, then if E is the total intensity of γ-radiation inside the lead front due to a point source of unit intensity at P,

$$E=K'\int_0^{2\pi}\int_0^a \frac{\cos\varphi\,.\,e^{-\mu t/\cos\varphi}\,.\,r\,.\,d\theta\,.\,dr.}{R^2}$$

Using the substitutions $R^2=d^2(1+k^2)$

$$k^2=(r^2-2ry\cos\theta+y^2)/d^2$$

$$m=\mu t/2$$

$$K=K'e^{-\mu t}\,.\,/d^2$$

we have approximately

$$E=K\int_0^{2\pi}\int_0^a \frac{1-mk^2+\left(\frac{m}{4}+\frac{m^2}{2}\right)k^4}{(1+k^2)^{3/2}}\,.\,r\,.\,d\theta\,.\,dr.$$

Error $<$ 0·1 per cent. if $a<7$ cms. and $d>25$ cms.

And writing $n=\left(\frac{m}{4}+\frac{m^2}{2}\right)$

$$f=3/2+m$$

$$g=\frac{15}{8}+\frac{3m}{2}+n$$

$$h=\frac{35}{16}+\frac{15m}{8}+\frac{3n}{2}$$

then $E=2K\int_0^{\pi}\int_0^a \{1-f\,.\,k^2+g\,.\,k^4-h\,.\,k^6\}\,r\,.\,d\theta\,.\,dr.$

Putting $T=y/d$

$$A=1-\left(\frac{f}{2}\,.\,\frac{a^2}{d^2}-\frac{g}{3}\,.\,\frac{a^4}{d^4}+\frac{h}{4}\,.\,\frac{a^6}{d^6}\right)$$

$$B=f-2g\,.\,\frac{a^2}{d^2}+3h\,.\,\frac{a^4}{d^4}$$

$$C=g-\frac{9h}{2}\,.\,\frac{a^2}{d^2}$$

$$D=h$$

we have $E=\pi a^2K\{A-BT^2+CT^4-DT^6\}$ . . . (4)

In the case considered

$a=7{\cdot}0$, $d=25{\cdot}0$, $\mu=0{\cdot}5$ and $t=0{\cdot}5$,

so that

$$E=\pi a^2K\{0{\cdot}94097-1{\cdot}3003T^2+1{\cdot}4766T^4-2{\cdot}4805T^6\}$$

For a value of y as large as 6·5, $2{\cdot}4805T^6=0{\cdot}00077$, so that the last term may usually be neglected with an error less than 0·1 per cent.

UNIFORM LINE SOURCE.

The expression may readily be integrated to obtain the correction for a uniform line source along OP (Fig. 1). In the case when the line source is bisected by OC, the percentage correction will be found to be

$$\frac{100\{BT^2/3-CT^4/5\}}{A-\{BT^2/3-CT^4/5\}} \quad \ldots\ldots\ldots \quad (5)$$

UNIFORM RECTANGULAR LAMINAR SOURCE PERPENDICULAR TO THE AXIS OC.

From (4) we have that

$$E=\pi a^2K\{A-B'r^2+C'r^4\}$$

where

$$B'=B/d^2$$

$$C'=C/d^4$$

and r is the perpendicular distance of a point source of unit intensity from the axis OC. The last term of (4) is omitted as being usually negligible.

Taking rectangular co-ordinates x, y in a plane perpendicular to OC, and substituting $x^2+y^2=r^2$, we have as an expression for the total effect of a rectangular source of uniform intensity I per unit area

$$\pi a^2KI\int_{x_1}^{x_2}\int_{y_1}^{y_2}\{A-B'(x^2+y^2)+C'(x^2+y^2)^2\}\,.\,dx\,.\,dy.$$

which gives the percentage correction

$$\frac{100(B'R-C'S)}{AQ-(B'R-C'S)} \quad \ldots\ldots\ldots \quad (6)$$

where

$$Q=(x_2-x_1)(y_2-y_1)$$

$$R=\frac{1}{3}\{(x_2^3-x_1^3)(y_2-y_1)+(y_2^3-y_1^3)(x_2-x_1)\}$$

$$S=\left\{\frac{(x_2^5-x_1^5)}{5}(y_2-y_1)+\frac{2}{9}(x_2^3-x_1^3)(y_2^3-y_1^3)+\frac{(y_2^5-y_1^5)}{5}(x_2-x_1)\right\}$$

In most practical cases the centre of the rectangular laminar will lie on OC, so that $x_1=-x_2$ and $y_1=-y_2$, and the expressions for Q, R and S will be considerably shortened.

UNIFORM SQUARE LAMINAR SOURCE CENTRALLY PLACED PERPENDICULAR TO THE AXIS OC.

In this case, putting $x_1=y_1=0$, and $x_2=y_2=b$, the side of the square being $2b$, expression (6) for the percentage correction becomes

$$\frac{100\left\{\frac{2}{3}B'\,.\,b^2-\frac{28}{45}C'\,.\,b^4\right\}}{\mathrm{A}-\left\{\frac{2}{3}B'\,.\,b^2-\frac{28}{45}C'\,.\,b^4\right\}} \quad \ldots\ldots\ldots \quad (6a)$$

UNIFORM CIRCULAR DISC SOURCE WITH CENTRE DISTANT C FROM THE AXIS OC, AND IN A PLANE PERPENDICULAR TO OC.

The effect due to a point source of unit intensity distant p from the axis is

$$E=\pi a^2K\{A-B'p^2+C'p^4\}$$

so that if I is the intensity of the source per unit area, we have for the total effect of the disc source, taking polar co-ordinates about the centre of the disc, the expression

$$\pi a^2KI\int_0^{2\pi}\int_0^{R}\{A-B'p^2+C'p^4\}r\,.\,d\theta\,.\,dr.$$

where $p^2=c^2+r^2-2cr\cos\theta$, and R is the radius of the disc, which gives as the percentage correction

$$\frac{100(B'U-C'V)}{A-(B'U-C'V)}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$U=c^2+R^2/2$$

$$V=c^4+2c^2R^2+R^4/3$$

If the centre of the disc lies on OC the percentage correction becomes

$$\frac{100(B'\,.\,R^2/2-C'\,.\,R^4/3)}{A-(B'\,.\,R^2/2-C'\,.\,R^4/3)}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

UNIFORM CYLINDRICAL SOURCE, THE AXIS OF THE CYLINDER CUTTING OC AT RIGHT ANGLES.

If I is the intensity per unit volume of the cylindrical source, then from (4) the total ionization effect produced by the source is given by

$$2\int_0^{\pi}\int_0^{B}\int_0^{L}\left\{\pi a^2KI\left(A-B\,.\,\frac{c^2}{d^2}+C\,.\,\frac{c^4}{d^4}\right)\right\}r\,.\,d\theta\,.\,dr\,.\,dy.\quad . \quad . \quad . \quad . \quad . \quad (9)$$

where, referring to Fig. 2, c is the perpendicular distance of the volume element at W from OC, the term involving D being regarded as negligible.

From the figure we have

$$d=d_0-z\,;\quad z=r\cos\theta$$

$$c^2=y^2+x^2=y^2+r^2-z^2$$

Substituting for c in terms of y, r and $\cos\theta$, and using the expansions of reciprocal powers of d in terms of d_0 and $r\cos\theta$, expression (9) may be integrated to the required degree of approximation. Terms have been neglected which on integration affect the accuracy of the expression to about 0·1 per cent. for the case when $a=7{\cdot}25$, $d=25$, $\mu=0{\cdot}5$, $t=0{\cdot}5$ and $R\ngtr 3$. The percentage correction may then be expressed by

$$\frac{100\{B_0''\,.\,T_0^2/3-C_0''\,.\,T_0^4/5\}}{A_0''-\{B_0''\,.\,T_0^2/3-C_0''\,.\,T_0^4/5\}}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where

$$A_0''=A_0-\frac{R^2}{4d_0^2}\left\{f+\frac{3fa^2}{2d_0^2}-\frac{2ga^2}{d_0^2}\right\}$$

$$B_0''=B_0+\frac{R^2}{2d_0^2}\left\{\frac{3f}{2}-g\right\}$$

$$C_0''=C_0$$

The suffix "$_0$" to A, B and C indicates that in their values given in (4) d_0 is to be understood for d.

If $R \ngtr 1$, the values of a, d, μ and t being the same as before, sufficient accuracy may be obtained by putting

$$A_0'' = A_0 - \frac{fR^2}{4d_0^2}$$

$$B_0'' = B_0$$

$$C_0'' = C_0$$

SHORT UNIFORM CYLINDRICAL SOURCE, THE AXIS COINCIDING WITH *OC*.

If the intensity of the source is I per unit volume, we have from (8) that the total ionization effect of the source is proportional to

$$\int_0^L \{A - B' . R^2/2 + C' . R^4/3\} dz$$

where L is the length of the cylinder and R its radius. Substituting $d = d_0 - z$ in the expressions for A, B' and C', and using expansions for reciprocal powers of d as before, the expression obtained for the percentage correction is of the form

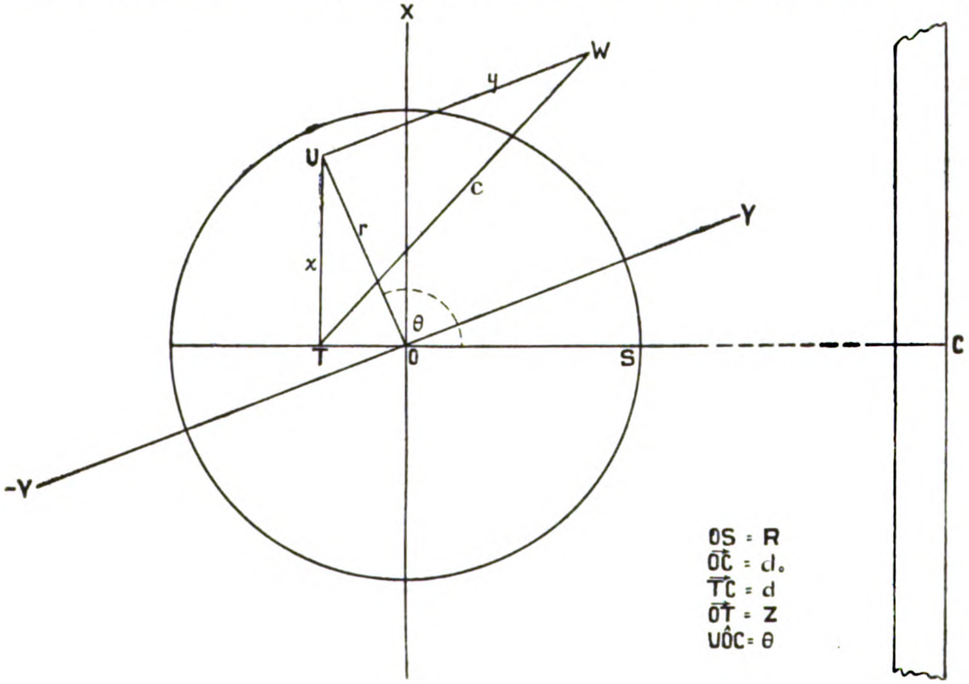


FIG. 2.

$$\frac{100\{B_L . T_0^2/2 - C_L . T_0^4/3\}}{A_L - \{B_L . T_0^2/2 - C_L . T_0^4/3\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $T_0 = R/d_0$.

If L is not greater than 0·5 and R is not greater than "a," the values of "a," d, μ and t being the same as before, we have with sufficient accuracy—i.e., 0·1 per cent.,

$$A_L=1-\left\{\frac{f\,.\,a^2}{d_0^2}\left(1+\frac{L}{d_0}\right)-\frac{g\,.\,a^4}{3d_0^4}+\frac{ha^6}{8d_0^6}\right\}$$

$$B_L=\left\{f\left(1+\frac{L}{d_0}\right)-\frac{2ga^2}{d_0^2}+\frac{3ha^4}{d_0^4}\right\}$$

$$C_L=g-\frac{9h}{2}\,.\,\frac{a^2}{d_0^2}$$

UNIFORM SOURCE IN THE FORM OF A SHORT PRISM OF SQUARE SECTION, THE AXIS COINCIDING WITH OC.

We have from (6a) that the total ionization effect of the source is proportional to

$$\int_0^L\left\{A-\frac{2}{3}B'b^2+\frac{28}{45}C'b^4\right\}dz$$

where the side of the prism is $2b$ and its length is L. In the same way as for (11), the expression obtained for the percentage correction is

$$\frac{100\left\{\frac{2}{3}B_LT_0^2-\frac{28}{45}C_LT_0^4\right\}}{A_L-\left\{\frac{2}{3}B_LT_0^2-\frac{28}{45}C_LT_0^4\right\}}\quad\ldots\ldots\ldots\quad(12)$$

where $T_0=b/d_0$ and A_L, B_L and C_L have the same values as before.

SHORT UNIFORM CYLINDRICAL SOURCE, THE AXIS COINCIDING WITH OC, AND THE LINEAR ABSORPTION COEFFICIENT IN THE CYLINDER BEING ν'.

If t' is the depth of an element of the source $I\,.\,r\,.\,d\theta\,.\,dr\,.\,dt'$ behind the face of the cylinder nearer the ionization chamber, the expression for the total ionization effect of the source will be

$$\int_0^{2\pi}\int_0^R\int_0^Z I\,.\,r\,.\,d\theta\,.\,dr\,.\,dt'\,.\,K'\int_0^{2\pi}\int_0^a\frac{\cos\varphi\,.\,e^{-\frac{\mu t+\nu' t'}{\cos\varphi}}}{R^2}\,.\,r\,.\,d\theta\,.\,dr.$$

This expression will only be accurate when the diameter of the cylinder is equal to that of the ionization chamber, but providing the length of the cylinder is small compared with its diameter the error involved will have a negligible effect on the percentage correction. The value of ν' for ZnS, BaCl, $BaSO_4$ and $BaCO_3$ will not exceed 0·1 cm.$^{-1}$, so that in these cases we have with sufficient accuracy

$$\int_0^{2\pi}\int_0^R I\,.\,r\,.\,d\theta\,.\,dr\,.\,K'\int_0^{2\pi}\int_0^a\frac{\cos\,.\,\varphi\,.\,e^{-\frac{\mu t+\nu' t'}{\cos\varphi}}}{R^2}\,.\,r\,.\,d\theta\,.\,dr.$$

$$=\pi^2R^2a^2KI\left\{A'''-B'''\,.\,\frac{R^2}{2}+C'''\,.\,\frac{R^4}{3}\right\}.\quad\ldots\text{ from }(8)$$

where
$$A'''=1-\left\{\frac{f'.a^2}{2(d+t')^2}-\frac{g'a^4}{3(d+t')^4}+\frac{h'a^6}{4(d+t')^6}\right\}$$

$$B'''=\frac{f'}{(d+t')^2}-\frac{2g'a^2}{(d+t')^4}+\frac{3h'a^4}{(d+t')^6}$$

$$C'''=\frac{g'}{(d+t')^4}-\frac{9h'a^2}{2(d+t')^6}$$

and
$$f'=f+v't'$$

$$g'=g+\frac{7v't'}{4}$$

$$h'=h+\frac{9v't'}{4}$$

Integrating with regard to t' from $t'=o$ to $t'=z$, we obtain for the percentage correction

$$\frac{100.\{B_zT^2/2-C_zT^4/3\}}{A_z-\{B_zT^2/2-C_zT^4/3\}}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

where
$$A_z=1-\left(\frac{f_za^2}{2d^2}-\frac{g_za^4}{3d^4}+\frac{h_za^6}{4d^6}\right)$$

$$B_z=f_z-\frac{2g_za^2}{d^2}+\frac{3h_za^4}{d^4}$$

$$C_z=g_z-\frac{9h_za^2}{2d^2}$$

$$f_z=f\left(1-\frac{z}{d}\right)+\frac{v'z}{2}$$

$$g_z=g\left(1-\frac{2z}{d}\right)+\frac{7v'z}{8}$$

$$h_z=h$$

and
$$\mathrm{T}=R/d$$

assuming as before that the length of the cylinder, here denoted by z, is $\ngtr$ 3·5 cm.

UNIFORM SOURCE IN THE FORM OF A SHORT PRISM OF SQUARE SECTION, THE AXIS COINCIDING WITH *OC*, AND THE LINEAR ABSORPTION COEFFICIENT IN THE PRISM BEING v'.

In the same way as (13) is obtained from (8) we obtain from (6a) for the percentage correction

$$\frac{100\left\{\frac{2}{3}B_z.\mathrm{T}^2-\frac{28}{45}C_z.\mathrm{T}^4\right\}}{A_z-\left\{\frac{2}{3}B_z.\mathrm{T}^2-\frac{28}{45}C_z.\mathrm{T}^4\right\}}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

where A_z, B_z and C_z have the same values as in (13).

CORRECTION FOR THE EFFECT OF SCATTERED RADIATION.

The measured ionization effect E'_y, due to a point source distant y from the axis, will consist of two parts, E_y due to direct radiation and E_s due to radiation scattered from surrounding objects. If the materials producing the greater part of the scattering are at a distance from the source, large compared with y, then, to a first approximation, E_s will be independent of y and constant for a given distance from the ionization chamber.

We have therefore

$$E_y'=E_y+E_s \text{ and } E_0'=E_0+E_s$$

and

$$\frac{E_0'-E_y'}{E_y'}=\frac{E_0-E_y}{E_y}\times\frac{1}{1+E_s/E_y}$$

If

$$\frac{E_0'-E_y'}{E_y'}=c' \text{ and } \frac{E_0-E_y}{E_y}=c$$

we have

$$\frac{E_s}{E_y}=\frac{c-c'}{c'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where **100*c*′** is the percentage correction determined experimentally for a point source distant y from the axis, and $100c$ is the percentage correction as calculated. In this way an estimation of the amount of scattered radiation may be readily made.

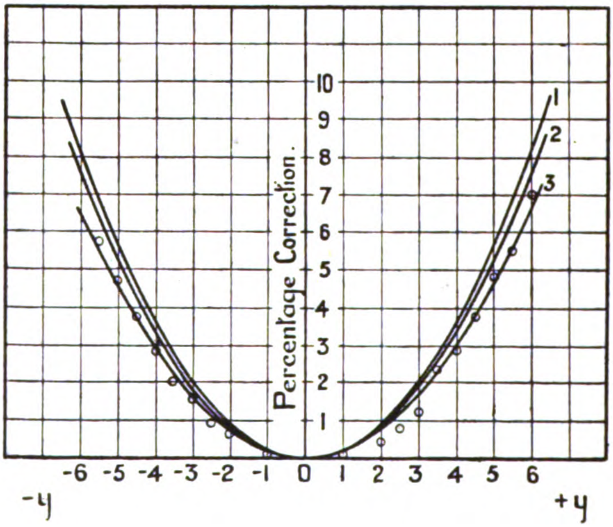


FIG. 3.

Since E_s is constant, we may put $E_s=K_0 \, . \, E_0$, so that

$$c'=\frac{c}{1+K_0.E_0/E_y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and

$$K_0=\frac{c-c'}{c'(c+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In Fig. 3 the percentage correction is shown for different values of y for the case of a point source when $a=7{\cdot}0$, $d=25$, $\mu=0{\cdot}5$, $t=0{\cdot}5$.

Curve 1 is obtained from

$$100c=\frac{100\{BT^2-CT^4\}}{A-\{BT^2-CT^4\}} \quad \text{. . . . . from (4)}$$

Curve 2 is obtained from

$$100c=\frac{100\{LT^2-MT^4\}}{\text{Vers } \varphi-\{LT^2-MT^4\}} \quad \text{. . . . . . from (2)}$$

Curve 3 is obtained from Curve 1 using the relation

$$100c'=\frac{100c}{1+K_0 \cdot \frac{E_0}{E_y}} \quad \text{. . . . . from (16)}$$

with $K_0=0{\cdot}21$.

The experimental points indicated were obtained using as source a small thin-walled glass tube containing radium sulphate. In the case of sulphate the greater part of the active deposit appears to reside on the sulphate powder, and only a small part on the glass walls of the tube, so that with the sulphate shaken to one end of the tube an approximation to a point source could be obtained. With a view to reducing the effect of scattered radiation, the experiment was carried out in the centre of the room, a light table being used to support the apparatus and the ionization chamber and radium tube were supported rather more than twelve inches above the table. The holder for the radium tube was a strip of thin stiff paper about twelve inches long folded to a V-section and supported at the ends by two light wooden rods.

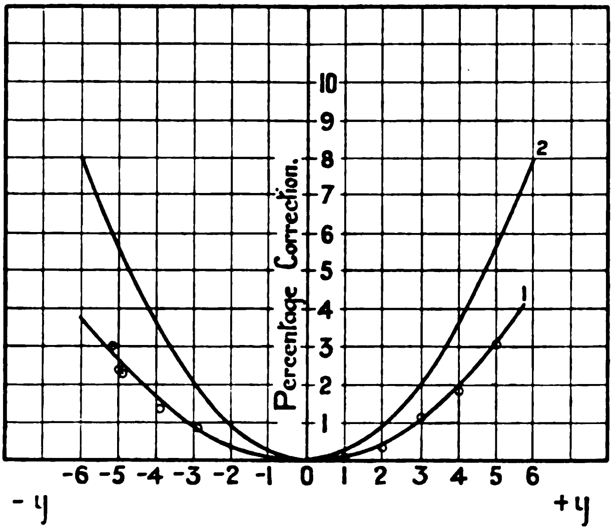


FIG. 4.

In Fig. 4 the percentage correction is shown for different values of y for the case of a point source when $a=7{\cdot}25$, $d=25$, $\mu=0{\cdot}5$, $t=0{\cdot}5$.

Curve 1 is drawn through the experimental points.

Curve 2 is calculated from

$$100c=\frac{100\{BT^2-CT^4\}}{A-\{BT^2-CT^4\}}\cdot\ .\ .\ .\ .\ .\ .\ .\ .\quad \text{from (4)}$$

where $A=0{\cdot}93721$, $B=1{\cdot}2821$, $C=1{\cdot}4130$.

In this case the experiment was carried out on a radium bench parallel and close to one of the walls of the room, a wooden holder being used to support the radium tube. Negative values of y indicate positions on the wall side of the axis OC. The effect of scattered radiation is considerably more marked than in Fig. 3, and the proximity of the wall is sufficient to cause some asymmetry of the experimental curve.

In Table I the percentage correction is shown for different values of d with tubes of different lengths, placed centrally and perpendicular to OC, for the case when $a=7{\cdot}25$, $\mu=0{\cdot}5$ and $t=0{\cdot}5$. The values (which are calculated from 10) are for tubes having diameters not greater than 2 cms., no allowance being made for the effect of scattered radiation.

TABLE I.—*Percentage Correction.*

Diameter of tube not greater than 2 cms.

Distance in cms. (d)	Length of tube in cms.									
	12	11	10	9	8	7	6	5	4	3
25	2·6	2·2	1·8	1·5	1·2	0·9	0·6	0·4	0·3	0·2
30	1·9	1·6	1·3	1·1	0·8	0·7	0·5	0·3	0·2	0·1
35	1·4	1·2	1·0	0·8	0·6	0·5	0·4	0·3	0·2	
40	1·1	0·9	0·8	0·6	0·5	0·4	0·3	0·2	0·1	
45	0·9	0·8	0·6	0·5	0·4	0·3	0·2	0·2	0·1	
50	0·7	0·6	0·5	0·4	0·3	0·3	0·2	0·1		
55	0·6	0·5	0·4	0·3	0·3	0·2	0·2	0·1		
60	0·5	0·4	0·4	0·3	0·2	0·2	0·1			
65	0·4	0·4	0·3	0·2	0·2	0·1	0·1			
70	0·4	0·3	0·3	0·2	0·2	0·1				
75	0·3	0·3	0·2	0·2	0·1	0·1				
80	0·3	0·2	0·2	0·2	0·1					
85	0·3	0·2	0·2	0·1	0·1					
90	0·2	0·2	0·2	0·1	0·1					
95	0·2	0·2	0·1	0·1						
100	0·2	0·2	0·1	0·1						
110	0·2	0·1	0·1							
120	0·1	0·1								
130	0·1									

In conclusion, the author wishes to thank Dr. E. A. Owen for his kind advice and interest in this work.

SUMMARY.

Formulæ are given for obliquity corrections in radium estimation applicable in the following cases :—

1. Point source.
2. Uniform line source.
3. Uniform rectangular laminar source perpendicular to *OC*.
4. Uniform square laminar source centrally placed perpendicular to *OC*.
5. Uniform circular disc source in a plane perpendicular to *OC*.
6. Uniform cylindrical source, axis cutting *OC* at right angles.
7. Short uniform cylindrical source, axis coinciding with *OC*.
8. Uniform source in the form of a short prism of square section, axis coinciding with *OC*.

9 and 10. As (7) and (8), with correction for absorption in the source included.

OC is the axis (produced) of the ionization chamber, assumed cylindrical in form.

DISCUSSION.

Prof. O. W. **Richardson** complimented the author on a very careful piece of work, which would be of value in industrial measurements.

Dr. E. A. **Owen** said that investigators using radium will be grateful for the Paper, which works out fully the most interesting case—that in which the tube is at right angles to the radium bench—and also the effect of scattering. Radium is usually estimated in a comparatively small room, and near the walls. It would appear that by keeping at a distance from walls the effect of scattering can be reduced by about one-half, and it is very useful to know the exact figures.

Mr. A. F. **Dufton** (communicated) : Mr. Backhurst's experimental results indicate that, owing to the effect of scattered radiation, the formulæ propounded are perhaps more of academic than of practical interest. In practice, the comparison of two radium preparations can be so effected that the obliquity correction is obviated. For example, in comparison with either a tube 4 in. long or a plaque 3 in. in diameter, a concentrated preparation can be placed 1 in. from the axis. At a reasonable distance from the ionisation chamber this displacement compensates for the distribution of the radium and the application of a correction is avoided.

Author's reply (communicated) : From the experiments it will be seen that in order to be able to calculate the obliquity correction with a reasonable degree of accuracy without the necessity of any recourse to experiment, it is important to reduce the amount of scattered radiation to a minimum. Under the conditions of experiment obtaining in Fig. 3 for example, the error introduced by the effect of scattered radiation in the case of a tube 12 cm. long, placed centrally perpendicular to the axis, would amount to about ½ per cent., this being approximately one-third of the error for a point source at 6 cm. from the axis. Should it be necessary to allow for the effect of scattered radiation, the constant K_0 must be determined, for which, however, one experimental value is sufficient.

Mr. Dufton suggests that the obliquity correction may be obviated by displacing the standard radium source a suitable distance from the axis. One of the disadvantages of this method is that to obtain the same degree of accuracy afforded by reference to a table of corrections, the comparison experiments must occupy a considerably longer time unless the equivalent position of the standard source is correctly calculated for each case. It is clear that the terms involving T^4 in a formula such as No. 5 may often be neglected, and the correction taken as proportional to the square of the distance from the axis, but a linear relationship, such as he assumes, will not be nearly such a good approximation, as a glance at Fig. 3 will at once show. In the case he gives of a tube 4 in. long, the standard source being placed 1 in. from the axis, an error of about 0·4 per cent. would be made if the measurements were carried out at 25 cm. from an ionisation chamber of 14·5 cm. diameter and in the ideal case of no scattering. If scattering exists to a large extent as in the experiment illustrated in Fig. 4, the error made would be about 0·3 per cent. To reduce this error to about 0·1 per cent. the measurements could be carried out at 50 cm. distance, but the time for each observation would be four times as long. At 25 cm. distance an observation on a weak source seldom occupies less than 1 minute and frequently more than 2 minutes. From 60 to 120 observations are commonly taken on the two sources being compared. so that in order to obtain results to an equivalent degree of acuracy Mr. Dufton would have to spend from 3 to 12 hours longer by his method.

Two of the main objects of the Paper have been to show how a table may be compiled by reference to which such a loss of time may be avoided and how a moderate degree of scattering may be allowed for with fair accuracy. Mr. Dufton would appear to regard such considerations as mainly of " academic " importance.

XXIX.—VISCOSITY OF WATER AT LOW RATES OF FLOW DETERMINED COMPARATIVELY BY A METHOD OF THERMAL CONVECTION.

By ALBERT GRIFFITHS, *D.Sc.*, Professor of Physics, Birkbeck College, and P. C. VINCENT, *B.Sc.*, Research Student, Birkbeck College.

Received February 26, 1926.

ABSTRACT.

The Paper describes a method of determining the coefficient of viscosity of water by measuring the rate of convective flow in a long capillary tube, the driving head being obtained by the difference in density due to a difference of temperature between two vertical columns of water.

The results are in agreement with the conclusion reached in a previous Paper by Dr. Constance H. Griffiths and one of us—*viz.*, that the viscosity of water at low rates of shear in glass tubes is apparently no different from that at high rates.

The novel features of the Paper appear to be (1) the method of obtaining the driving head; (2) the new method of introducing a coloured index in a closed capillary circuit, and an improved method of reading its position; (3) the almost complete elimination of what may be called the thermometric effect as distinct from the convective effect; (4) the elimination of the small residual thermometric effect from the final calculations.

THIS Paper describes a method of determining the coefficient of viscosity of water at low rates of shear by measuring the flow due to thermal convection in a closed circuit. This circuit consists essentially of a modified rectangle, composed of two short wide vertical tubes and two long horizontal capillary tubes, and the flow is caused by a difference of temperature between the two vertical tubes. The method gives results consistent to a fraction of one per cent.

Each series of horizontal capillary tubes was, in the first place, standardized or calibrated by measuring the flows due to heads of water of the order of 60 cms.; and the rate of shear at the boundary of the capillary tubes was of the order of 120 radians per second. In standardizing these tubes Hosking's values* for the coefficient of viscosity of water were taken as correct.

The rate of shear at the boundary in the convective experiments was, in one experiment, as low as 0·012 radians per second; and the effective driving head for the upper and lower sets of tubes in series was of the order of 0·014 cms. of water.

The method is essentially comparative, and it involves the knowledge of the relation between the density and temperature of water.

A diagrammatic sketch of the apparatus is shown in Fig. 1. AB and CD are the vertical arms of the rectangle, and E and F are the long horizontal capillary arms. E and F are each about 19 metres long, and they are of a vertical distance of about 18 cms. apart.

AB and CD are placed in glass accumulator tanks L and M respectively. The tank L is heated electrically, and a convective current proceeds from A to C and from D to B.

X and Y, each of which comprises a pair of three-way taps, are index-introducers—i.e., they enable short columns of a feeble uranine solution to be introduced into the capillary tubes; the linear movements with respect to time of these short coloured columns along the calibrated capillary tubes give the rate of flow of the convective current.

---

* Phil. Mag., Vol. 18, p. 262 (1909).

The vertical tubes *AB* and *CD* have a considerable volume-capacity, and if the circuit were absolutely closed the changes in volume of the water due to variations in temperature might damage the apparatus and cause a leak; but, quite apart from any damage to the apparatus, the changes in volume may cause a movement of the water, which is not usually called a convection-current and which may be called a "thermometric movement." This thermometric movement in *E* and *F* may be eliminated by the broad tubes *G* and *H*, which run from the wide vertical tubes into an open glass tank *K*, which is partially filled with water. These broad tubes are provided with taps *I* and *J*. If changes of temperature occur in *AB* only, say, then thermometric movements in the capillary tubes are prevented by opening *I* and closing *J*, for any expansion or contraction is satisfied by a movement into and out of *K*.

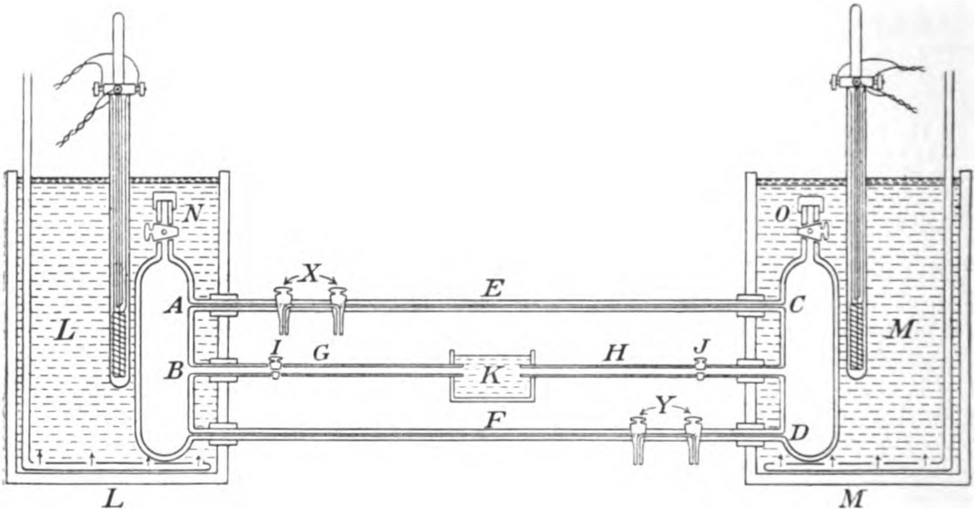


Fig. 1.

If the tap *J* is closed and changes of temperature occur in *CD* as well as in *AB*, then there are thermometric movements in the capillary tubes; but by using two coloured indexes in the rectangular circuit, one travelling from *A* to *C*, the other from *D* to *B*, the effects due to the thermometric movement are eliminated from the final calculations; for if an expansion, say, occurs in *CD* an increase in speed from *D* to *B* is balanced in the calculations by a decrease in speed from *A* to *C*.

Results may be, and have been, obtained with both the taps *I* and *J* open; but with this arrangement the apparatus can hardly be said to be functioning as a simple closed circuit.

The water in the high-temperature tank *L* and the low-temperature tank *M* was kept thoroughly stirred by means of bubbles of air. A piece of compo tubing was so shaped that it fitted inside the tank parallel and close to one vertical edge, and parallel and close to three bottom horizontal edges. The further end of the tubing was sealed. Fine holes about 6 inches apart were bored along the length of the tubing at the bottom of the tank. The open end of the tubing was connected to a water pump which was so arranged that a gentle stream of air bubbles was forced through the water in the tanks.

Surface evaporation of the water in a tank was made very small by covering the surface with a layer of medicinal paraffin oil. Without this coating the changes of temperature caused by the evaporation due to the stirring was excessive and troublesome.

The vertical parts *AB* and *CD* have attached at their upper ends tubes *N* and *O* provided with stop-cocks. These tubes are for convenience in filling the apparatus. *N* and *O* are provided with indiarubber seals.

The temperature of the tank *M* was adjusted so as to be approximately that of the air of the room.

The capillary tubes were kept at a uniform temperature by an arrangement which cannot be explained with the aid of the diagrammatic sketch, for the actual shape of the apparatus was decidedly different from that shown in Fig. 1. The arrangement is explained later.

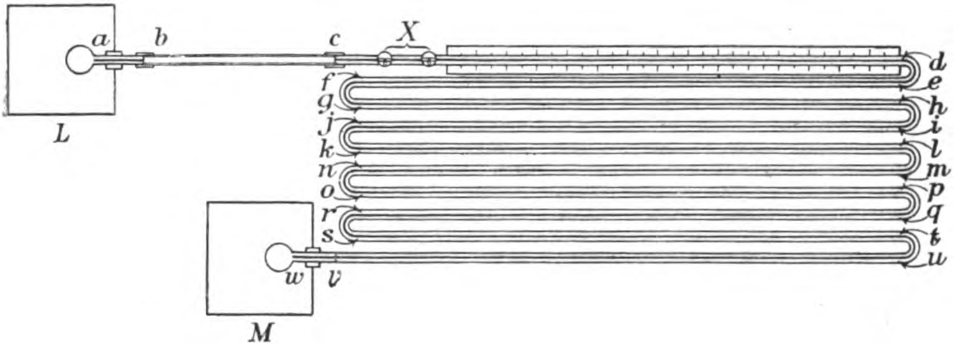


FIG. 2.

Fig. 2 shows, by means of a rough plan, the actual arrangement of the apparatus and the way the capillary tubes are connected to the tanks *L* and *M*.

The upper capillary tube is made of 12 lengths, *cd*, *ef*, . . . *uv*, each about 160 cms. long. These lengths are connected together by glass U-tubes with the aid of transparent indiarubber tubing, the ends of the tubes being ground flat, so as to make the fitting good. The series of tubes is supported on a stout wooden frame, the level of which can be adjusted by levelling screws. The tube *cd* is provided with an index introducer *X*. Under *cd* is fixed a black paper scale with division marks drawn with Chinese white. The scale is black to make the faint fluorescent light of the index easily visible. The tube *cd* is calibrated so far as volume-capacity is concerned by obtaining the mass of mercury occupying various lengths of the tube and dividing by the density of the mercury. Thus the volume in cubic centimetres between the zero and any division of the scale is known.

The high-temperature tank *L* radiates heat, and it is therefore advisable to place it at a considerable distance (50 cms. in many of the experiments recorded) from the series of capillary tubes. The connecting tube *bc* is of wide bore, and in consequence the viscous resistance to the flow of water along it is negligible; and therefore the difference between its temperature and that of the capillary circuit may be neglected altogether, and it is not necessary to determine the variation of temperature along it—i.e., along the tube *bc*.

The tube *ab* is of capillary bore. It passes through an indiarubber stopper that is inserted in a hole, which has been sand-blasted through the walls of the tank. It is short; and therefore no correction is required for its temperature.

The lower series of capillary tubes is arranged in an analogous manner to the upper one. It, in particular, has a tube analogous to *cd*, which has been carefully calibrated, and which contains an index-introducer.

The whole apparatus is in a thermostat-room; but it was found in earlier experiments that the high-temperature tank *L* caused excessive variations of the temperature in the neighbourhood of the series of capillary tubes, especially in those parts of the tubes nearest the heater. In the experiments recorded a uniform temperature throughout the length of both series of tubes was obtained by means of an electric fan. This fan blew a stream of air at the general temperature of the thermostat-room towards the hot tank parallel to and through the system of tubes.

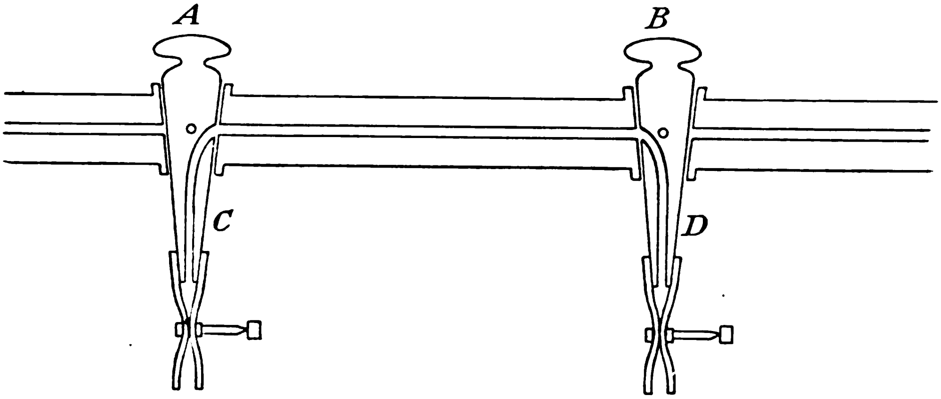


FIG. 3.

This uniformity of temperature is important, for a change of one degree centigrade causes the coefficient of viscosity of water, over the range of the experiments, to vary by more than 2 per cent.

It would probably be an improvement to have the capillary tubes in a large, well-stirred water-bath; but this would involve many incidental changes in the apparatus, and would, moreover, be expensive.

METHOD OF INTRODUCING A COLOURED INDEX INTO A CALIBRATED TUBE.

A sketch indicating the method of introducing coloured indexes into the upper and lower series of capillary tubes is shown in Fig. 3.

Two three-way taps *A* and *B* are placed at a convenient distance apart (say 4 cms.). The openings *C* and *D* are provided with indiarubber tubes which can be sealed by means of clips.

To introduce an index a feeble solution of uranine is passed from *C* to *D*. The indiarubber tubes are now sealed with the clips and the tap-plugs are each turned through 90°.

The indiarubber seals to *C* and *D* are of vital importance, for without them there is generally sufficient leakage from one or both of the plugs to spoil an experiment.

In the case of the index-introducers used in the experiments described in this Paper, the taps *A* and *B* were at such a distance apart that the procedure described above could be adopted. If their distance apart should be too great a coloured index of convenient length may be obtained by allowing the flow to take place until a requisite length of coloured liquid has emerged from the space between the taps. The rear part of the coloured liquid may then be washed out by turning the tap-plugs *A* and *B* through 90°, undoing the screw clips, and sending a stream of water from *C* to *D*. Obviously, the tap-plugs *A* and *B* must now be turned back through 90°, and *C* and *D* again sealed.

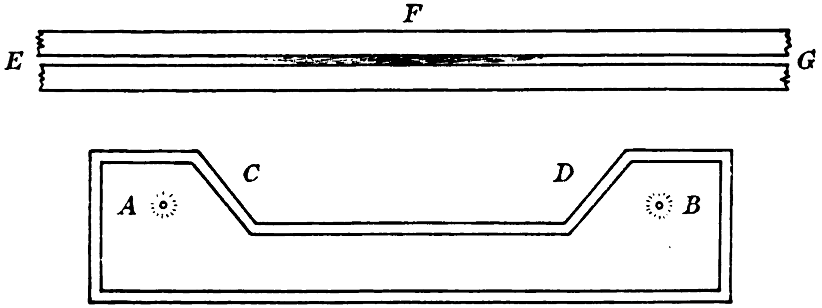


Fig. 4.

In the experiments recorded in this Paper the strength of the uranine solution was 0·5 grams to the litre.

Method of Reading the Coloured Index.

An improved method, involving the use of two incandescent lamps, was used to read the position of the coloured index.

In earlier unrecorded experiments the illumination consisted of a solitary lamp placed in a box which was provided with a window of cobalt glass. When the lamp was in a symmetrical position, as it should be, with regard to the coloured index, and the eyes of the observer were held over the fluorescent index, discomfort in reading was caused by the relatively powerful reflection from the outer wall of the capillary tube.

The source of illumination in the experiments recorded in this Paper is shown in Fig. 4.

Two lamps *A* and *B* were contained in a box provided with cobalt glass windows *C* and *D*. The capillary tube is indicated by *EG*, the fluorescent index by *F*. The illuminating apparatus is arranged in a symmetrical position with regard to the index, and it is clear that if the eyes of the observer are above *F* the rays from *A* and *B* through *C* and *D* respectively, which strike the outer wall of the capillary tube in the neighbourhood of the index, are reflected to right and left, and do not disturb the observer. The fluorescent light from the uranine is scattered in all directions, and can therefore be readily seen.

STANDARDIZATION OF EACH SERIES OF CAPILLARY TUBES AT A RATE OF SHEAR OF ABOUT 140 RADIANS PER SEC.

Let V_1=the volume-flow along the upper series (*AEC* in Fig. 1) in cubic centimetres per second.

V_2=the volume-flow along the lower series, *DFB*, in cubic centimetres per second.

P_1=the difference of pressure between the ends of *AEC* in dynes per square centimetre.

P_2=the difference of pressure between the ends of *DFB* in dynes per square centimetre.

φ=the temperature of the water in the capillary tubes.

$\mu\phi$=the coefficient of viscosity at $\varphi^0 c$, obtained from Hosking's formula.*

For standardizing the tube use is made of constants K_1 and K_2 defined by

$$P_1=\mu\varphi K_1 V_1 \quad \text{. . . . . (1)}$$

$$P_2=\mu\varphi K_2 V_2 \quad \text{. . . . . (2)}$$

(it may be incidentally mentioned that $K=\frac{8l}{\pi a^4}$, where l is the length of a capillary tube and a the radius of the bore.)

The details of the apparatus used to standardize the capillary tubes are of no particular interest. The method is not an unusual one, and is sufficiently indicated by the figures given below.

Let t=time in seconds.

h_0=head of water in cms. when $t=0$.

h=head of water in cms. when $t=t$ secs.

ρ=density of water at temperature of experiment.

F=total volume-flow in time t in c.c.

Then it can be proved that

$$K=\frac{\rho g(h_0-h)t}{F\mu\varphi\ \log_e \frac{h_0}{h_1}}$$

As an example, consider the upper series of tubes. In one experiment the details were as follows:—h_0=69·98 cms., h=65·07 cms., t=2,580 secs., ρ=0·999 gm./cm.^{3}, F=140·457, φ=16^0·08, $\mu\varphi$=0·011124.

The values of K_1 and K_2 only vary very slightly with the temperature—about 2 parts in 100,000 per degree. They may be taken as constants.

The average value of $K_1=1{\cdot}0942\times10^8$.

" " $K_2=1{\cdot}5320\times10^8$.

The average rate of shear at the boundary is given by $\frac{4F}{\pi a^3 t}$, and was of the order of 140 radians per second.

---

* Phil. Mag., Vol. 18, p. 262 (1909).

THEORY OF THE FLOW DUE TO THERMAL CONVECTION.

Let T = the temperature of the high temperature tank L (*see* Fig. 5).
t = the temperature of the low-temperature tank M.
θ = the temperature of the capillary tubes.
H = the vertical distance in cms. between the centre of the capillary tubes near the high temperature tank L.
h = the vertical distance in cms. between the centres of the capillary tubes near the low temperature tank M.
v_1 = the volume-flow in cc. per sec. along AEC.
v_2 = the volume-flow in cc. per sec. along DFB.
ρ_T = the density of water at T°C.
ρ_t = density of water at t°C.
ρ_θ = density of water at θ°C.
η_θ = the coefficient of viscosity of water at θ°C.
p_a = the pressure at A in dynes per sq. cm.
p_b = ,, ,, B ,, ,,
p_c = ,, ,, C ,, ,,
p_d = ,, ,, D ,, ,,

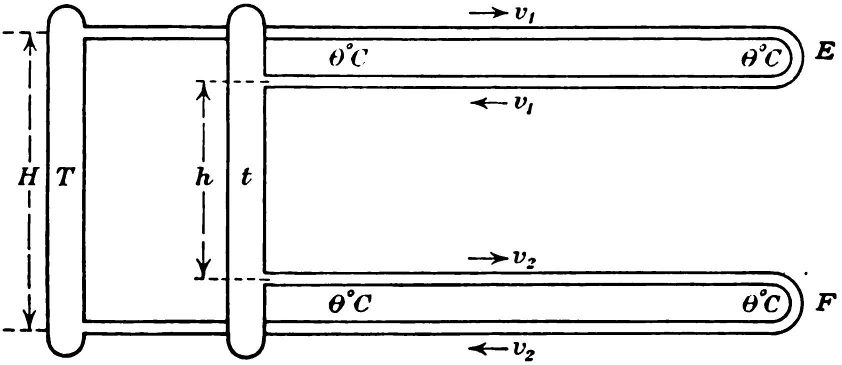


FIG. 5.

If the series of tubes E (Figs. 1 and 5) were absolutely horizontal, then $(p_a - p_c)$— i.e., the excess of the pressure at A above that at B would equal $\eta_\theta K_1 v_1$, as suggested by equation (1). If, however, the tubes are not horizontal, then, if A is at a height y_a above a given horizontal plane, not shown in the figures, the excess of the pressure is given by the equation

$$p_a - p_c = \eta_\theta K_1 v_1 + (y_c - y_a)\,\rho_\theta g \quad \dots\dots\dots \quad (3)$$

Similarly, where p_d and p_b have obvious meanings

$$p_d - p_b = \eta_\theta K_2 v_2 + (y_b - y_d)\,\rho_\theta g \quad \dots\dots\dots \quad (4)$$

Since the tubes AB and CD are very wide, the viscous resistance in them may be neglected, and hydrostatical considerations give

$$p_b - p_a = g\,\rho_T H \quad \dots\dots\dots\dots\dots \quad (5)$$

$$p_d - p_c = g\,\rho_t h \quad \dots\dots\dots\dots\dots \quad (6)$$

adding corresponding sides of (3) and (4), and making use of (5) and (6), we obtain

$$\eta_\theta = \frac{g\,\rho_t h - g\,\rho_T H + g\,\rho_\theta H - g\,\rho_\theta h}{K_1 v_1 + K_2 v_2}$$

By a little algebraic manipulation the equation may be put in the form

$$\eta_\theta = \frac{g(\rho_t - \rho_T)\,H + g(\rho_\theta - \rho_t)\,(H - h)}{K_1 v_1 + K_2 v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This form of expression for η_θ is useful as indicating the effect of the horizontal tubes,.etc., not being exactly horizontal.

If the tubes are exactly horizontal, $H=h$, and the second term in the numerator of equation (7) vanishes: for $(H-h)=0$.

If $H=|=h$, but the temperature of the tubes is the same as that of the low temperature tank, the second term again vanishes; for $\rho_\theta - \rho_t = 0$.

In practice in the experiments recorded in this Paper both $(\rho_t - \rho_T)$ and $(H-h)$ are small, and their product is so exceedingly small that the second term in the numerator may be neglected, and it is sufficiently exact to write

$$\eta_\theta = \frac{g(\rho_t - \rho_T)H}{K_1 v_1 + K_2 v_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It may be mentioned that generally v_1 does not differ greatly from v_2. If there is no thermometric motion v_1 should equal v_2.

In the course of a long experiment, when T, t, v_1 and v_2 vary, $(\rho_t - \rho_T)$ should be taken as the average value of the difference between the two densities, and v_1 and v_2 should be average rates of volume-flow per second.

With the small variations in temperature associated with the present experiments, to a sufficient degree of accuracy, (1) the average value of $(\rho_t - \rho_T)$, and (2) the value of ρ at the average value of t minus the value of ρ at the average value of T are equal.

Some of the calculations involved are suggested by the following Table I, which gives the figures for the series of observations denoted Experiment 1.

TABLE I.

θ	T	ρ_T	t	ρ	$(\rho_t - \rho_T)$	Time
17·67°C.	43·14°C.	0·991012	17·66°C.	0·998684	0·00767153	12½
17·63	43·18	0·990998	17·69	0·998678	0·00768120	12¾
17·59	43·21	0·990983	17·72	0·998673	0·00768970	13
17·57	43·30	0·990946	17·69	0·998677	0·00773135	13¼
17·55	43·40	0·990908	17·67	0·998681	0·00777322	13½
17·55	43·46	0·990883	17·80	0·998658	0·00777508	13¾
17·62	43·54	0·990850	17·81	0·998656	0·00780598	14
17·67	43·66	0·990801	17·85	0·998649	0·00784796	14¼
17·75	43·68	0·990793	17·88	0·998644	0·00785096	14½
17·75	43·73	0·990771	17·90	0·998639	0·00786819	14¾
17·78	43·77	0·990756	17·93	0·998634	0·00787803	15
17·84	43·80	0·990744	17·94	0·998633	0·00788944	15¼
17·86	43·82	0·990735	18·00	0·998622	0·00788715	15½
17·82	43·84	0·990725	18·01	0·998621	0·00789567	15¾
17·85	43·86	0·990717	18·04	0·998614	0·00789746	16
17·85	43·88	0·990711	18·07	0·998609	0·00789859	16¼
17·85	43·91	0·990698	18·09	0·998605	0·00790638	16½
17·84	43·92	0·990694	18·13	0·998597	0·00790300	16¾
17·85	43·94	0·990684	18·15	0·998593	0·00790932	17
17·83	43·98	0·990667	18·17	0·998590	0·00792270	17¼
17·86	43·97	0·990674	18·21	0·998583	0·00790936	17½
17·92	43·96	0·990676	18·25	0·998578	0·00790267	17¾
17·85	43·97	0·990672	18·25	0·998574	0·00790224	18
17·90	43·94	0·990684	18·28	0·998569	0·00788509	18¼
17·90	43·94	0·990684	18·28	0·998569	0·00788509	18½
17·77	43·71	0·990779	17·98	0·998625	0·00784665	Averag

(1) Average value of $(\rho_t - \rho_T) = 0{\cdot}00784665$.

(2) Value of ρ at average value of t minus the value of ρ at average value of $T = 0{\cdot}00784749$.

The figures for the densities are interpolated from tables given in the 1905 edition of Landolt-Bornstein Physikalisch-Chemische Tabellen.

It may be noted that the error involved in taking the average value of $(\rho_t - \rho_T)$ as the difference between the densities at the average temperatures is of the order of 0·01 per cent. Thus the arithmetical calculations may be abbreviated enormously. They could be still further abbreviated for approximate work by first calculating the average platinum thermometer temperatures and transforming these to the hydrogen-thermometer scale.

DETAILS OF THE CONVECTIVE EXPERIMENTS.

The distilled water in the apparatus was in each case boiled in a copper vessel, then put under an exhaust pump, and finally a trace of copper sulphate was added to the water. This treatment was to sterilise the water and to preserve it from the development of fungoid growths.

The temperatures of the tanks *L* and *M* were read every quarter of an hour by means of platinum thermometers, when the convective flow lasted five or six hours, and were read every two hours (day and night) when the experiment lasted days. The platinum thermometer temperatures were reduced to the gas-thermometer scale in the usual way.

The temperature of the air in the neighbourhood of the capillary tubes was read about the same time as the tank temperatures by means of mercury thermometers. The same thermometers were used during the standardization of the capillary tubes at rapid flow, and, as the method is a comparative one, any small absolute error or correction in these thermometers is of little importance.

The Griffiths-Callendar bridge which was used in conjunction with the platinum thermometers, and the telescopes which were used for reading the mercury thermometers, were placed behind a screen; and thus the thermal effect of the observers, which had caused considerable difficulty in preliminary experiments, was made negligible.

EXPERIMENT 1.—SEPTEMBER 22, 1925.

The apparatus was cleaned before the experiment, the duration of which was about six hours. The apparatus was not quite as indicated in the diagram, the long tube *bc* being missing; but the distance from the capillary systems to the heating tank *L* was sufficiently great.

EXPERIMENT 2.—NOVEMBER 5, 1925.

New water was introduced in the convective apparatus and the experiment lasted about five hours. The arrangement was the same as in Experiment 1.

EXPERIMENT 3.—NOVEMBER 6, 1925.

The same water was used as in Experiment 2, and the conditions were the same.

EXPERIMENT 4.—DECEMBER 7, 1925.

The apparatus was cleaned and new water was added. The arrangement was like that described in the text, with the addition of a cork mat placed so as to protect the low temperature tank from the radiation emitted by the high temperature tank. The experiment lasted five hours.

EXPERIMENT 5.—DECEMBER 18-20, 1925.

The same water was used as in Experiment 4, and the conditions were the same, except that there was a much smaller difference of temperature between the two tanks, and thus a much reduced rate of flow.

It may be noted that the average excess is of the order of magnitude of minus one-tenth per cent.

The values of the viscosity at low rates of shear (see Table II) differ from those at high rates of shear by less than would be expected from the errors to which the various measurements are liable; and there is no suggestion that the viscosity of water at low rates of shear in glass tubes is different from that at high rates of shear.

TABLE II.—*Summary of Experimental Results.*

Date	Sept. 22.	Nov. 5.	Nov. 6.	Dec. 17.	Dec. 18-20.
Time in secs. ...	21,229	18,960	19,140	18,060	200,872
Rate of flow, v_1 ...	$4{\cdot}914 \times 10^{-5}$	$4{\cdot}708 \times 10^{-5}$	$6{\cdot}163 \times 10^{-5}$	$4{\cdot}266 \times 10^{-5}$	$4{\cdot}852 \times 10^{-6}$
Rate of flow, v_2 ...	$4{\cdot}904 \times 10^{-5}$	$4{\cdot}585 \times 10^{-5}$	$6{\cdot}089 \times 10^{-5}$	$4{\cdot}353 \times 10^{-5}$	$4{\cdot}951 \times 10^{-6}$
Average value of θ...	17·77°C.	17·38	17·61	17·93	16·77
K_1	$1{\cdot}0942 \times 10^{8}$	$1{\cdot}0942 \times 10^{8}$	$1{\cdot}0942 \times 10^{8}$	$1{\cdot}0942 \times 10^{8}$	$1{\cdot}0942 \times 10^{8}$
K_2	$1{\cdot}5320 \times 10^{8}$	$1{\cdot}5320 \times 10^{8}$	$1{\cdot}5320 \times 10^{8}$	$1{\cdot}5320 \times 10^{8}$	$1{\cdot}5320 \times 10^{8}$
Average value of T	43·71°C.	42·346°C.	48·292°C.	41·087°C.	20·972°C.
Average value of t ...	17·98°C.	17·377°C.	17·781°C.	17·645°C.	16·799°C.
Average value of $(\rho_t - \rho_T)$	$7{\cdot}847 \times 10^{-3}$	$7{\cdot}328 \times 10^{-3}$	$9{\cdot}817 \times 10^{-3}$	$6{\cdot}861 \times 10^{-3}$	$8{\cdot}108 \times 10^{-4}$
H in cms.	17·78	17·78	17·78	17·80	17·80
Approx. rate of shear in radians per sec.	0·13	0·13	0·16	0·12	0·013
Hosking's values of coefficient of viscosity	0·01062	0·01074	0·01068	0·01058	0·01090
Experimental values of coefficient of viscosity	0·01062	0·01067	0·01065	0·01056	0·01095
Excess above Hosking's	0·0 p.c.	−0·7 p.c.	−0·3 p.c.	−0·2 p.c.	+0·5 p.c.

This conclusion is the same as that arrived at by a different method,* in which the effective driving head was mainly due to the difference between the density of a weak uranine solution and that of pure water.

To the authors the chief points of the present work appear to be :—

(1) The proof that a considerable degree of control has been obtained in the production of a small calculable pressure-head of different values in a closed circuit containing water, by means of a difference of temperature between two vertical columns of water.

(2) The absence of any suggestion (in accordance with numerous unpublished observations with a preliminary form of the apparatus) that the viscosity of water at low rates of shear is different from that at high rates of shear.

(3) The arrangement for minimizing the thermometric movement in the circuit.

(4) The method of using two coloured indexes in appropriate parts of the circuit, thus eliminating the effects due to the slight thermometric movement from the final calculation.

(5) The new device by introducing a coloured index in a closed circuit, and the special type of lamp for reading the position of the coloured index.

In conclusion, the authors wish gratefully to acknowledge the assistance of Messrs. H. G. Bell, H. Broan, F. Staley and G. Steeden, and to express their appreciation of the suggestions and help of Dr. Constance H. Griffiths.

DISCUSSION.

Prof. O. W. **Richardson** said that the authors had used an ingenious method of getting a controlled flow of water at an extremely slow rate, which might have many useful applications in research.

Prof. A. **Griffiths** said that in an earlier investigation, made in conjunction with Dr. Constance Griffiths, irregularities had been found which must be due either to temperature errors or to what had been called in the present Paper the " thermometric effect." This Paper helped to throw light on that subject, but the work described formed part of rather a long series of determinations, and he therefore felt that the Society had exhibited a certain amount of good nature in receiving it.

Mr. F. E. **Smith** said that, on the contrary, many Fellows of the Society had a great admiration for the extremely accurate and thorough work which was being carried out under Prof. Griffiths direction. Apparently nothing else of the same kind was being done in this country, and it was only by extensive experimentation that all the properties of liquids could be recorded.

Mr. L. F. **Richardson** : Sandström has stated that it is impossible for heat to produce a steady circulation unless the source of heat is at a level lower than that of the sink of heat. At first sight these experiments seem to contradict this statement, because the hot and cold vertical tubes are on the same level. But on consideration of the readings in Table II it is clear that the cooling occurred mainly near where the water entered the upper capillary, while the heating occurred mainly at the lower end of the warm vertical column. Thus there is no conflict with Sandström's statement.

---

* " Viscosity of Water at Low Rates of Shear," by Albert Griffiths and Constance H. Griffiths, Proc. Phys. Soc., Vol. 33, Part 4, June 15 (1921).

XXX.—THE PROPERTIES OF MUTUAL INDUCTANCE STANDARDS AT TELEPHONIC FREQUENCIES.

By L. HARTSHORN, *A.R.C.S.*, *B.Sc.*, *D.I.C.*,
Electrical Department, National Physical Laboratory.

Received March 2, 1926.

ABSTRACT.

It is well known that when a mutual inductance carries alternating current, the value of the effective mutual inductance varies with the frequency, and further that the secondary P.D. is not exactly in quadrature with the primary current. Thus certain frequency corrections are introduced into all alternating-current bridges in which a mutual inductance standard is used. An experimental investigation has been made of the actual magnitude of such corrections for mutual inductance standards of three types :—

(1) A stranded wire fixed standard, with spaced winding to minimise capacity effects.
(2) The Campbell variable mutual inductance standard.
(3) The Tinsley variable mutual inductance standard made in accordance with Butterworth's recommendations.

Values of the corrections are given for all these instruments under various conditions. It is shown that whereas the variation of mutual inductance with frequency is mainly due to capacity effects, dielectric losses in the insulation, or alternating current conductance, play an important part in the determination of the phase defect, the impurity being found to be proportional to a power of the frequency higher than the second, over the telephonic range of frequency.

INTRODUCTORY.

MUTUAL inductance standards may be used in alternating-current bridge work for making a great variety of measurements. They may be used for measuring capacity or inductance, in which case they may be regarded as standards of reactance. They may also be used in potentiometer methods for measuring phase angles, e.g., the power factor of a condenser, or the phase angle of a standard shunt. In such cases they may be regarded as standards of phase angle.

In using a mutual inductance as a standard of phase angle we make use of the fact that when alternating current passes through the primary coil, the E.M.F. induced in the secondary coil is exactly in quadrature with the current in the primary coil. The quantity we are concerned with in bridge and potentiometer measurements is not so much the E.M.F. induced in the secondary coil, as the potential difference between its terminals. In a perfect mutual inductance the P.D. between the terminals of the secondary coil on open circuit would be equal and opposite to the E.M.F. induced in that coil, but in practice, owing to the existence of capacity and eddy-current effects in the secondary coil, and also capacity effects between the primary and secondary coils, the P.D. between the secondary-coil terminals is not exactly equal and opposite to the induced E.M.F., but differs somewhat from this both in magnitude and phase. Further, as mentioned above, the E.M.F. induced in the secondary coil by a definite current flowing through the primary coil is exactly in quadrature with that current, but owing to distributed capacity and eddy-current effects in the primary coil and between the two coils, the current is not exactly the same in every element of the primary coil. The current we measure in practice is the current flowing into one primary terminal and out of the other. If earth-capacity effects are not suitably distributed these two currents will not be exactly equal, but here earth-capacity effects will not be considered, since they are not so much a property of the instrument itself as of its position and potential distribution. Accordingly, we shall consider the primary current I_p as flowing into one primary terminal and out of the other. It is obvious from what has been said that the P.D. (V_s) between the secondary terminals on open circuit will not usually be in quadrature with I_p. We may write

$$V_s=(\sigma+jM\omega)I_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where M is the effective mutual inductance, σ is the impurity, $\omega/2\pi$=frequency, and j is the operator rotating through a right angle. We may regard $\theta=\tan^{-1}\frac{M\omega}{\sigma}$ as being the phase angle of such a mutual inductance. It is very nearly equal to 90 deg. The small angle $\delta=90$ deg. $-\theta=\tan^{-1}\frac{\sigma}{M\omega}$ may be regarded as the phase defect of the instrument. This Paper gives an account of an experimental investigation into the properties of actual mutual inductance standards of various types with special reference to the impurity and change of effective mutual inductance at the higher telephonic frequencies.

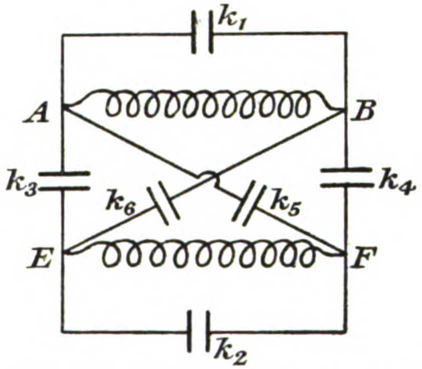


FIG. 1.—EQUIVALENT NETWORK FOR MUTUAL INDUCTANCE STANDARD.

GENERAL THEORETICAL CONSIDERATIONS.

Butterworth* has investigated mathematically the effect of eddy currents and capacity effects on the effective mutual inductance and impurity of two coils. Let AB, EF (Fig. 1) be the two coils. As an approximation the distributed-capacity effects in the system are represented by the capacities k_1, k_2, k_3, k_4, k_5, k_6, which are regarded as concentrated at the ends of the coils. In order to simplify the problem further, suppose the two coils have a common point, say, AE. The capacity k_3 is now short circuited and disappears, k_1 and k_6 are thrown in parallel and may be represented by a single capacity C_1, k_2 and k_5 similarly form the single capacity C_2, and we have the system of Fig. 2, in which $C_{12}=k_4$. Butterworth shows that this system possesses the following properties.

---

* Butterworth, Proc. Phys. Soc., Vol. 33, p. 312 (1921).

Let L_1R_1 be the resistance and self-inductance of the primary coil, L_2R_2 those of the secondary coil, and M_0 the true or geometrical mutual inductance between them, then the effective mutual inductance and impurity as defined by Equation (1) are given by

$$M=M_0+C_{12}R_1R_2+\omega^2\{C_1L_1M_0+C_2L_2M_0-C_{12}(L_1-M_0)(L_2-M_0)\} \quad . \; . \; . \quad (2)$$

$$\sigma=\omega^2[C_1R_1M_0+C_2R_2M_0-C_{12}\{R_1(L_2-M_0)+R_2(L_1-M_0)\}] \quad . \; . \; . \; . \; . \; . \quad (3)$$

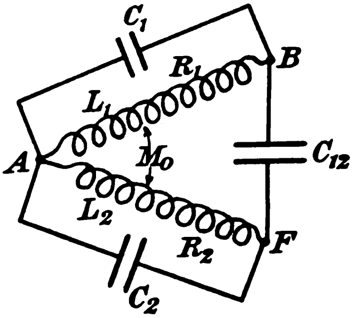


FIG. 2.—SIMPLIFIED NETWORK WHEN THE TWO COILS HAVE ONE POINT COMMON.

These expressions only hold when the capacity effects are comparatively small, i.e., when terms such as $C_1\omega$ are small compared with those such as $\frac{1}{L_1\omega}$, small quantities of the second order being negligible. Further the sign of M_0 may be either positive or negative. If the direction of winding of the two coils is such that when current flows in at one open end, through the coils, and out of the other, the mutual inductance opposes the self-inductance, M_0 must be taken as positive. If the mutual inductance assists the self-inductance under these conditions, M_0 must be taken as negative. We shall accordingly speak of positive and negative mutual inductances. In order that this definition may be consistent with equation (1), we must suppose that the secondary potential difference V_s is reckoned in a definite direction, viz., when I_p flows towards the common point, V_s is also directed towards the common point (*see* Fig. 3), i.e., in the diagram F is considered to be at a higher potential than A. If the secondary coil is contained in a closed circuit, so that the induced E.M.F. produces a current, this current will flow from F to A in the

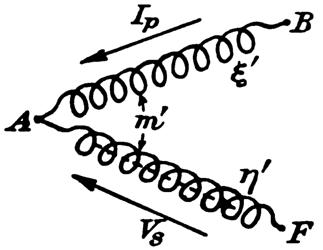


FIG. 3.—EQUIVALENT SYSTEM OF IMPEDANCE OPERATORS.

part of the circuit external to the coil, and from A to F through the coil, i.e., the E.M.F. induced in the coil must be regarded as acting in the direction AF, as shown by the dotted arrow.

Equation (2) gives the change of effective mutual inductance with frequency as a result of capacity effects. At very low frequencies the effective mutual inductance is equal to the geometrical mutual inductance M_0, since the term involving ω^2 is then negligible, while the term $C_{12}R_1R_2$ is nearly always negligible. As the frequency increases, M increases by an amount

$$\triangle M = \omega^2 \{C_1L_1M_0 + C_2L_2M_0 - C_{12}(L_1 - M_0)(L_2 - M_0)\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For convenience $\frac{\triangle M}{M_0}$ is often referred to as the frequency coefficient of the mutual inductance. Thus

$$\text{Frequency coefficient} = \frac{\triangle M}{M_0} = \omega^2 \left\{ C_1L_1 + C_2L_2 - C_{12} \, . \, \frac{(L_1 - M_0)(L_2 - M_0)}{M_0} \right\} \quad . \quad . \quad (5)$$

We may regard $L_1C_1\omega^2$ as the frequency coefficient due to the self-capacity of the primary coil, and $L_2C_2\omega^2$ that due to the self-capacity of the secondary coil. Both these terms are always positive. The frequency coefficient due to the mutual capacity between the two coils is $-C_{12}\frac{(L_1 - M_0)(L_2 - M_0)\omega^2}{M_0}$, and this term may be either positive or negative, depending on the relative value of L_1, L_2 and M_0. When M_0 is negative, this term is always positive, and is numerically equal to $C_{12}\frac{(L_1 + M_0)(L_2 + M_0)}{M_0}$. When M_0 is positive, and $L_1 > M_0$, $L_2 > M_0$, which is commonly the case in practice, the term is negative, and thus the frequency coefficient due to mutual capacity opposes that due to self-capacity. If $L_1 > M_0 > L_2$, the term is positive, but is numerically much smaller than the case in which M_0 is negative, provided C_{12} is the same in the two cases. Thus a positive mutual inductance has a much smaller frequency coefficient than a negative one, the capacities being the same in the two cases. This is an important practical point, since a mutual inductance standard can readily be changed from positive to negative by changing the common point, and in some bridges M may be of either sign. In such cases it is nearly always preferable to use a positive M.

Similar considerations apply to the phase defect due to capacity

$$\delta_c = \tan^{-1} \frac{\sigma_c}{M\omega} = \frac{\sigma_c}{M\omega} \text{ (approx.).}$$

Equation (3) gives

$$\delta_c = R_1C_1\omega + R_2C_2\omega - C_{12}\left\{ R_1\frac{(L_2 - M_0)}{M_0}\omega + R_2\frac{(L_1 - M_0)\omega}{M_0} \right\} \quad . \quad . \quad . \quad (6)$$

and from this it follows that $\frac{\sigma_c}{M\omega}$ is always positive for a negative mutual inductance. In the case of a positive mutual inductance, the phase defect due to mutual capacity opposes that due to self-capacity, when $L_2 > M_0$ and $L_1 > M_0$, and in all cases the impurity and phase defect of a positive mutual inductance are less than those in a negative mutual inductance, if the capacities are the same in the two cases. When we are dealing with one particular pair of coils, the sign of M may be changed by simply changing the common point; but by reference to Figs. 1 and 2 we see that this change also alters the values of C_1, C_2 and C_{12}, unless the whole arrangement is perfectly symmetrical, which is not probable. Thus, when the sign of M is changed, the frequency coefficient and impurity are liable to change merely on account of the alteration in the values of C_1, C_2 and C_{12}. Nevertheless, in almost all the cases met with in practice, the negative connection possesses much the larger frequency coefficient and impurity.

Butterworth* has also shown that the effect of eddy currents in the coils is to introduce another component of impurity σ_e. This may be positive or negative, depending on the method of winding of the coils; but, in general, standards of mutual inductance are wound with stranded wire, and the effects of eddy currents are of less importance than those due to capacity.

METHODS OF MEASUREMENT.

In setting out to measure the properties of a number of typical standards of mutual inductance, it is important to have a method of measurement of effective mutual inductance and impurity at various frequencies, which is rapid in operation and which can be used for a wide range of frequencies. The methods used have been described in a previous Paper.† Two alternating-current potentiometer methods are there described. By means of one method two mutual inductances of the same sign, and not necessarily of the same magnitude, can be compared for impurity and effective mutual inductance at any desired frequency. The other method, the simplest possible, permits the comparison of two mutual inductances, equal in magnitude but opposite in sign. In both cases the impurity of one mutual inductance is given directly in ohms, provided the impurity of the other is negligibly small, or at any rate known. The quantities which it was desired to investigate were the frequency coefficient, or change of effective mutual inductance with frequency, and the impurity. The procedure was as follows: The instrument under test was connected in a circuit by means of which it could be balanced against a mutual inductance standard, which was known to possess a very small impurity and frequency coefficient. Balance was first obtained at a low frequency—say 100 cycles per second—using a vibration galvanometer as detector. At this low frequency the impurity of any ordinary mutual inductor is sensibly zero, and its effective mutual inductance is practically equal to its geometrical value M_0. The frequency was then raised to, say, 1,000 cycles, and a telephone was substituted for the vibration galvanometer as detector. The change to the higher frequency causes a change in the effective mutual inductance, and also introduces an impurity, and the arrangement is no longer balanced. The instruments tested were all variable mutual inductors, and thus balance at the higher frequency was obtained by reducing the mutual inductance reading by an amount $\triangle M$, and at the same time altering the impurity adjustment r. If the impurity and frequency coefficient of the standard are negligible, then $\triangle M$ gives at once the change of mutual inductance with frequency of the instrument under test, whilst the impurity is obtained at once from the change in the value of *r*. The frequency was then again raised, and the values of $\triangle M$ and impurity found for the higher frequency, and so on. In this way the frequency coefficient and impurity of the instrument were readily obtained for the whole range of telephonic frequencies.

---

* Butterworth, loc. cit.

† Journal of Scientific Instruments, Vol. 2, p. 145 (1925).

In order to work the method successfully, it is necessary to have a high frequency standard of mutual inductance—that is to say, a standard whose properties at high frequency are as nearly as possible the same as at low frequencies. For this purpose two coils such as are used in radio frequency work were frequently used. These coils were wound of highly stranded wire, so that eddy current effects were very small, and they were "slice" wound, so that capacity effects were reduced to a minimum. Two such coils of the same diameter and placed side by side possess a mutual inductance which is very nearly pure and invariable with frequency over the telephonic range. The value of the mutual inductance is conveniently varied by moving one coil away from the other along their common axis. They must not, of course, be turned so that a portion of the winding of one coil comes into the strongest part of the field of the other, otherwise eddy current effects will be increased. For testing 10mH mutual inductometers, a fixed standard mutual inductance designed by Mr. D. W. Dye was used. The coils are wound on an ebonite frame of cylindrical form. This is "slice" wound with stranded wire (size 7/36's), the whole forming a coil of self inductance about 50·5mH. The winding is broken at two points, thus dividing it into three sections (Fig. 4). The middle section serves as the secondary coil, while the other two coils connected in series form the primary. Thus the secondary is sandwiched in between the two halves of the primary, thereby securing a comparatively high coupling coefficient, and thus enabling the 10mH of mutual inductance to be obtained with correspondingly less wire.

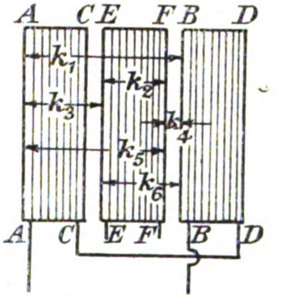


FIG. 4.—ARRANGEMENT OF COILS IN HIGH FREQUENCY MUTUAL INDUCTANCE STANDARD.

DETERMINATION OF RESIDUAL EFFECTS IN THE STANDARD.

For many purposes this standard may be regarded as a perfectly pure mutual inductance of constant value. There will, however, be certain small capacity effects even at telephonic frequencies. In particular, the mutual capacities are likely to be rather high on account of the closeness of coupling, and these mutual capacities affect the values of C_1, C_2 and C_{12}, as previously explained. Eddy current effects also may not be absolutely negligible. An idea of the magnitude of these residual effects was obtained in the following manner.

(*a*) *Self-capacity Measurements at Radio Frequencies.*

Let one primary terminal be connected to one of the secondary terminals, so that the system of Fig. 2 is obtained. Butterworth[*] has shown that this is equivalent to the system of Fig. 5, where X, Y and Z are vector impedances (assuming we are dealing with alternating currents of frequency $\omega/2\pi$), such that the following relations are satisfied,

$$X,\ Y,\ Z=\frac{x+\alpha\mu,\ y+\beta\mu,\ z+\gamma\mu}{1+\alpha(y+z)+\beta(z+x)+\gamma(x+y)+\lambda\mu}$$

where

$$x=j\omega M_0=m,\quad y=R_1+jL_1\omega-jM_0\omega=l-m,\quad z=R_2+jL_2\omega-jM_0\omega=n-m,$$

$$\alpha=j\omega C_{12}\qquad \beta=j\omega C_2\qquad \gamma=j\omega C_1,$$

$$\mu=yz+zx+xy=ln-m^2\qquad \lambda=\beta\gamma+\gamma\alpha+\alpha\beta.$$

Let now a variable air condenser be connected across the primary coil (i.e., across AB in Fig. 2), and let the coil be loosely coupled to an oscillating circuit.

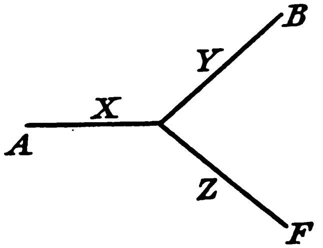


FIG. 5.—EQUIVALENT STAR CONNECTION.

Let the capacity of the added condenser be varied until the circuit resonates. If this is done for a number of frequencies, the relation between the added capacity and the corresponding resonating frequency can be obtained. The circuit will resonate at the frequency $\omega/2\pi$, such that the reactance of the oscillatory circuit formed is zero. This reactance consists of the reactance component of $X+Y$, together wtith that of the added condenser. From the above equations we obtain for the impedance $X+Y$,

$$X+Y=\frac{l+(\alpha+\beta)(ln-m^2)}{1+\alpha(l+n-2m)+\beta n+\gamma l+\lambda\mu}$$

The capacities C_1, C_2, C_{12} are small, and if the frequency is well below the self-resonance points of the various coils, the terms α, β, γ are small compared with $\frac{1}{l}$, $\frac{1}{m}$, $\frac{1}{n}$, i.e., terms such as $l\alpha$, $n\beta$, $l\gamma$, etc., are small compared with unity. If we neglect squares and products of such small quantities the above expression reduces to

$$X+Y=l-\alpha(l-m)^2-\beta m^2-\gamma l^2$$

$$=(R_1+jL_1\omega)-j\omega C_{12}[R_1+j(L_1-M_0)\omega]^2+j\omega C_2M_0^2\omega^2-j\omega C_{12}[R_1+jL_1\omega]^2.$$

The reactance component of this expression is

$$\omega[L_1-(C_1+C_{12})R_1^2+\omega^2\{C_1L_1^2+C_2M_0^2+C_{12}(L_1-M)^2\}].$$

---

[*] Butterworth, loc. cit.

The second term in this expression will be negligibly small for all reasonably good coils, and thus it can be omitted. The reactance of the added condenser is $-1/C\omega$. Thus, the condition for resonance is to a first approximation

$$\omega L_1\left[1+\omega^2\left\{C_1L_1+C_2\frac{M_0^2}{L_1}+C_{12}\frac{(L_1-M_0)^2}{L_1}\right\}\right]-\frac{1}{C\omega}=0,$$

or,

$$\frac{1}{\omega^2}=CL_1\left[1+\omega^2\left\{C_1L_1+C_2\frac{M_0^2}{L_1}+C_{12}\frac{(L_1-M_0)^2}{L_1}\right\}\right]$$

$$=L_1\left[C+\left\{C_1+C_2\frac{M_0^2}{L_1^2}+C_{12}\frac{(L_1-M_0)^2}{L_1^2}\right\}\right]\text{(approx.)},$$

since, in the second term, which is small, we may put $L_1C\omega^2=1$ with sufficient approximation. Thus, on plotting corresponding values of C and $1/\omega^2$ we get a straight line, which cuts the axis of C at the point $C=-C_p$, such that

$$C_p=C_1+C_2\frac{M_0^2}{L_1^2}+C_{12}\frac{(L_1-M_0)^2}{L_1^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and which is inclined to the C axis at an angle $\tan^{-1}L_1$. Evidently we may regard C_p as the effective self-capacity of the primary coil in the presence of the secondary, and may determine it in the manner indicated. Similarly the effective self-capacity of the secondary in the presence of the primary is given by

$$C_s=C_2+C_1\frac{M_0^2}{L_2^2}+C_{12}\frac{(L_2-M_0)^2}{M_0^2} \quad . \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and this may be determined in the same way. Finally, by connecting a variable condenser across *BF* (Fig. 2), and observing resonance points as before, the effective self-capacity of the primary and secondary in series (C_{ps}) may be determined. In this case the impedance of the coils between the terminals *BF* is given by

$$Y+Z=\frac{(l+n-2m)+(ln-m^2)(\beta+\gamma)}{1+a(l+n-2m)+\beta n+\gamma l+\lambda\mu}$$

Neglecting small quantities of the second order, this becomes

$$Y+Z=l_s+(\beta+\gamma)(ln-m^2)-al_s^2-\beta l_sn-\gamma l_sl,$$

where

$$l_s=y+z=l+n-2m=R_1+R_2+j\omega(L_1+L_2-2M_0).$$

The reactance component of the above impedance is

$$\omega[L_1+L_2-2M_0-\{C_1R_1^2+C_2R_2^2+C_{12}(R_1+R_2)^2\}+\omega^2\{C_1(L_1-M_0)^2$$
$$+C_2(L_2-M_0)^2+C_{12}(L_1+L_2-2M_0)^2\}].$$

Again, the term involving the resistance is negligibly small. Let C be the added capacity, and denote $L_1+L_2-2M_0$ by L_s, then the condition of resonance is

$$\frac{1}{\omega_1}=CL_s\left[1+\omega^2\left\{C_1\frac{(L_1-M_0)^2}{L_s}+C_2\frac{(L_2-M_0)^2}{L_s}+C_{12}L_s\right\}\right]$$

Thus, the self-capacity C_{ps} is given approximately by

$$C_{ps}=C_{12}+C_1\frac{(L_1-M_0)^2}{L_s^2}+C_2\frac{(L_2-M_0)^2}{L_s^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Thus, if L_1, L_2, and M_0 are known, and we measure C_p, C_s, and C_{ps}, in this way, we have three equations (7), (8) and (9), connecting C_1, C_{12}, and C_2, from which we can obtain their values.

Measurements were made in this way on the standard mutual inductance. Fig. 4 represents the geometry of this, while Fig. 1 represents its electrical constants. It is evident from Fig. 1 that four common points are possible, and by making the appropriate connections we obtain four different mutual inductances, two positive and two negative (the geometrical value is, of course, the same in each case).

The values observed for the various effective self-capacities are given in Table I. Substituting the values C_p, C_s, C_{ps} for any given common point in equations (7), (8), (9), and solving, the corresponding values of C_1, C_2, C_{12} were obtained. These are also given in Table I. It is interesting to note that the measured effective self-capacities are much greater when M_0 is negative than when it is positive. This is due to the large change in the numerical value of the terms (L_1-M_0), etc., in equations (7), (8) and (9). The component capacities C_1, C_2, C_{12}, are of the same order in the two cases. Immediately underneath each component capacity in Table I is given the combination of the various end-capacities in Fig. 1, which go to form that particular value of C_1, C_2 or C_{12}. From this it is at once evident that k_4, the capacity between B and F is the greatest of these end-capacities. The reason for this is apparent on inspection of Fig. 4; the points BF are the nearest together. The capacity k_5 between the points A and F is very much smaller, corresponding to their greater distance apart. It is also evident from the results in Table I that we cannot regard the capacities k_1, k_2, k_3, etc., as strictly additive when the connections are such as to throw them in parallel. The capacity C_1 is certainly largest when AF is the common point, in which case the large capacity k_4 is thrown across the primary.

TABLE I.

Sign of M.	Com. Pt.	Effective Self-capacities.			Component Capacities.		
		C_p	C_s	C_{ps}	C_1	C_2	C_{12}
		micro-microfarads.			micro-microfarads.		
+	AE	33	22	70	19 k_1+k_6	6 k_2+k_5	57 k_4
+	BF	16	32	32	5 k_1+k_5	25 k_2+k_6	30 k_3
−	AF	130	170	55	60 k_1+k_4	26 k_2+k_3	30 k_6
−	BE	57	100	26	21 k_1+k_3	60 k_2+k_4	8 k_5

$L_1=18{\cdot}5$ mH. $L_2=12{\cdot}0$ mH. $M_0=\pm10{\cdot}0$ mH.

but in general, where a capacity may be expected to be equal to the sum of two end-capacities, such as k_1+k_6, the value actually observed is smaller than the sum would be, judging by the values given for the single capacities k_3, k_4, k_5, k_6 as obtained from the values of C_1, C_2, C_{12}. This is partly explained by the fact that the capacities k_1, k_2 represent actions which take place across the same dielectric path; if they were to be strictly additive, each would have to be completely self-contained and shielded from the others.

Using these values of the various capacities, we can now calculate the values of σ and $\frac{\Delta M}{M_0}$, using equations (3) and (5). The values are given in Table II.

Table II.—*Frequency Coefficient and Impurity of High Frequency Fixed Mutual Inductance Standard.* (*Values calculated from capacities.*)

Sign of M.	Com. Pt.	Frequency.	$\frac{\Delta M}{M}$	σ (ohm)	$\frac{\sigma}{M\omega}$
+	AE	1,000 $\sim$	$0{\cdot}1\times10^{-4}$	$-0{\cdot}0001$	$-0{\cdot}2\times10^{-5}$
		2,000 $\sim$	$0{\cdot}5\times10^{-4}$	$-0{\cdot}0005$	$-0{\cdot}4\times10^{-5}$
		4,000 $\sim$	$2{\cdot}0\times10^{-4}$	$-0{\cdot}002$	$-0{\cdot}8\times10^{-5}$
+	BF	1,000	$0{\cdot}1\times10^{-4}$	$0{\cdot}000_0$	...
		2,000	$0{\cdot}6\times10^{-4}$	$0{\cdot}000_0$	...
		4,000	$2{\cdot}2\times10^{-4}$	$-0{\cdot}000_1$	-4×10^{-7}
—	AF	1,000	$1{\cdot}3\times10^{-4}$	$-0{\cdot}001_3$	$+2{\cdot}_1\times10^{-5}$
		2,000	$5{\cdot}_2\times10^{-4}$	$-0{\cdot}005$	$+4\times10^{-5}$
		4,000	$21{\cdot}_0\times10^{-4}$	$-0{\cdot}021$	$+8\times10^{-5}$
—	BE	1,000	$0{\cdot}_5\times10^{-4}$	$-0{\cdot}000_5$	$+0{\cdot}_8\times10^{-5}$
		2,000	$2{\cdot}_1\times10^{-4}$	$-0{\cdot}002$	$+1{\cdot}_6\times10^{-5}$
		4,000	$8{\cdot}_3\times10^{-4}$	$-0{\cdot}008$	$+3{\cdot}_2\times10^{-5}$

A check on the accuracy of these results was obtained in the following way. The standard was balanced against a variable mutual inductance of the same value using the simple comparison method, and readings of M and r noted, at a telephonic frequency. The connections to the primary and secondary coils of the standard were then each reversed, thus changing the common point, but not changing the sign of M. Balance could therefore again be obtained by adjusting the variable mutual inductance and also the impurity adjustment, just sufficiently to compensate for the differences in the impurity, and frequency change of the standard, for the two conditions of common points, i.e., the method is one of simple substitution since the frequency errors of the variable mutual inductance are sensibly the same in the two measurements. The results of such measurements are given in Table III, where $\left(\frac{\Delta M}{M_0}\right)_{AF}-\left(\frac{\Delta M}{M_0}\right)_{BE}$ represents the difference of the frequency corrections of the standard when the common points are AF and BE. Within the experimental error, the calculated and observed results are identical. In Table III, the values σ_{AF} and σ_{BE} must be considered as representing the impurity due to capacity effects only, since even in the case of the observed values, although eddy-current effects may also be appreciable, they may be expected to be the same in the two cases, and thus will cancel out on taking differences.

TABLE III.

Frequency.	$\left(\frac{\Delta M}{M}\right)_{AF}-\left(\frac{\Delta M}{M}\right)_{BE}$		$\sigma_{AF}-\sigma_{BE}$	
	Calculated.	Observed.	Calculated.	Observed.
1,000	$0\cdot_{8}\times 10^{-4}$	$0\cdot_{4}\times 10^{-4}$	$-0\cdot001$	$-0\cdot001$
2,000	$3\cdot_{1}\times 10^{-4}$	$2\cdot_{6}\times 10^{-4}$	$-0\cdot003$	$-0\cdot004$
4,000	$10\cdot_{8}\times 10^{-4}$	$11\cdot_{8}\times 10^{-4}$	$-0\cdot01_{1}$	$-0\cdot0_{2}$

The importance of eddy-current effects was estimated by the following experiments :—

(*b*) *Effective Resistance Measurements at Radio Frequencies.*

This method was used by Butterworth. The effective resistances of the coils at radio frequencies were measured by the ordinary resistance substitution method. As before, let the coils have a common point. Let R_1 be the effective resistance of the primary coil *AB* (Fig. 3) at any given frequency, let R_2 be the effective resistance of the secondary *AF* at the same frequency, then the resistance of the two coils in series (*BAF*) at the same frequency is $R_1+R_2-2\sigma$, where σ is the impurity of the mutual inductance between the coils at that frequency. Thus the total σ can be measured at a number of high frequencies, and the value at telephonic frequency obtained by extrapolation. Values obtained for the standard in this way are given in Table IV for two conditions of common point. Under the heading "impurity" column (*a*) gives the results obtained directly from the effective resistance measurements at the frequencies stated, column (*b*) gives the values obtained for various telephonic frequencies by extrapolation from the results in column (*a*). In column (*c*) the corresponding values of σ_c are given for comparison. These values are taken from Table II. The values in column (*a*) were found to vary as a higher power of the frequency than the square. This is probably due to dielectric losses in the insulation and will be referred to again later. The relation $\sigma=\sigma_0\omega^{2\cdot45}$ was found to hold approximately, and this was used in extrapolating. Even if the square law is assumed, however, the general conclusions are not affected, viz., that the component of σ due to eddy currents is less than 0·01 ohm at 4,000 ∿, and is therefore negligible for all practical purposes at telephonic frequencies. This follows at once from a comparison of the results in columns (*b*) and (*c*), and may be expected with the stranded wire used. Thus the values given in Table II may be taken as completely representing the behaviour of the standard at telephonic frequencies. When used as a positive mutual inductance, the impurity is negligible, while the value of the mutual inductance increases by 2 parts in 10,000 in passing from zero frequency (or, say, 100 ∿) to 4,000 ∿. When used as a negative mutual inductance, the impurity just becomes appreciable, whilst in going from 100 ∿ to 4,000 ∿, the mutual inductance increases by 2 parts in 1,000 in one case. The importance of knowing this is obvious, since in practice when testing a positive mutual inductance by the simple comparison method (the most satisfactory), the standard must be used as a negative mutual inductance.

TABLE IV.

Sign of M.	Com. Pt.	Frequency.	Impurity σ—ohms.		
			Observed. (*a*)	By extrapolation. (*b*)	From capacity measurements. (*c*)
+	*AE*	37,400	0·4		
		30,000	+0·2		
		20,000	$+0{\cdot}0_5$		
		4,000		$+0{\cdot}00_1$	−0·002
		2,000		$+0{\cdot}000_2$	$-0{\cdot}000_5$
		1,000		$+0{\cdot}000_0$	$-0{\cdot}000_1$
−	*AF*	25,000	−1·9		
		20,000	−1·0		
		10,000	−0·2		
		4,000		$-0{\cdot}02_1$	$-0{\cdot}02_1$
		2,000		−0·004	−0·005
		1,000		$-0{\cdot}000_3$	$-0{\cdot}001_3$

WORKING STANDARDS OF MUTUAL INDUCTANCE.

The Campbell inductometer, or variable mutual inductance standard, is very widely used for alternating-current bridge work, and accordingly it appeared to be advisable to determine its properties in some detail. Butterworth has given the frequency corrections for a 10mH instrument, at the top point of its scale, at 1,000 cycles; but, in addition to this, it is important to know how the frequency corrections vary with scale reading, change in common point, and also with the frequency itself. These points were investigated by comparison with the standard mutual inductance described above. This standard consisted of three coils (Fig. 4), and by using various combinations of these coils values of about 2mH, 5mH, 7mH and 10mH could be obtained. These were compared directly with the Campbell instrument set at the same reading. For the purposes of these experiments, it was usually sufficiently accurate to assume that the standard mutual inductance was perfect. Tables V and VI give the results obtained with the 10mH Campbell instrument. Table V gives the results for a common point which makes the mutual inductance positive, while Table VI gives values for a common point corresponding to a negative value for M. The following points are to be noted:—

(1) The increase of mutual inductance ($\triangle M$) with increase of frequency is always proportional to the square of the frequency within the experimental error.

(2) When the mutual inductance is positive, the fractional increase of mutual inductance with frequency is approximately constant (at any given frequency) over the whole range of the instrument. This does not hold when the mutual inductance is negative.

(3) The impurity σ in nearly every case increases more rapidly than the square of the frequency. Butterworth showed that the impurity due to capacity and eddy-current effects is proportional to the square of the frequency

under the conditions of these experiments. It is evident that there must be an additional component of impurity, which is proportional to a power of the frequency higher than the square. It is shown in a succeeding paragraph that this may be explained by dielectric losses in the insulating material in the coils.

(4) When the mutual inductance is positive the phase defect of this instrument is approximately constant at any given frequency for all readings of mutual inductance. This is very convenient in practice. For instance, in determining the power factor of a condenser by means of the Carey Foster bridge, using the instrument, the correction to be applied for the impurity of the mutual inductance will always be approximately the same for a given frequency. It is merely necessary to add the phase defect of the instrument to the observed value of the power factor.

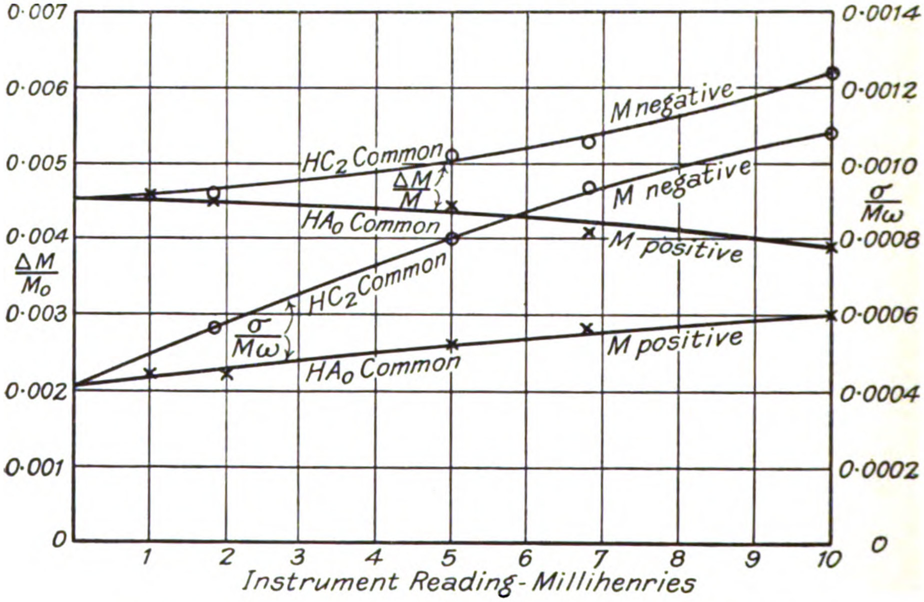


FIG. 6.—FREQUENCY CORRECTIONS OF 10MH CAMPBELL INDUCTOMETER.
Frequency = 2000 ∿.

(5) When the reading of the instrument is near the top of its scale, the frequency corrections for the negative connection are much larger than for the positive; but as the instrument reading becomes smaller the correction for the two methods of connection become more and more nearly equal. Fig. 6 shows this very clearly. There the frequency corrections at a frequency of 2,000 cycles are plotted against instrument reading for both methods of connection. The differences between the corrections for large values of M are evidently due to the effect of mutual capacity, as previously explained.

Tables V and VI gives the results for two common points. Two other common

TABLE V.—*Frequency Corrections of* 10mH *Campbell Inductometer.*
Common point HA_0. Mutual inductance positive.

Instrument reading M_0.	Frequency.	ΔM	σ (ohms).	$\frac{\Delta M}{M_0}$	$\frac{\sigma}{M\omega}$
1,000 μH	500	$0\cdot_3 \mu H$	$+0\cdot 000_4$	$2\cdot_9 \times 10^{-4}$	$0\cdot 0001_1$
	1,000	$1\cdot_2$	$+0\cdot 001_4$	$12\cdot_6 \times 10^{-4}$	$0\cdot 0002_2$
	1,500	$2\cdot_7$	$+0\cdot 003_2$	26×10^{-4}	$0\cdot 0003_3$
	2,000	$4\cdot_8$	$+0\cdot 005_7$	46×10^{-4}	$0\cdot 0004_4$
1,820	500	$0\cdot_5$	$+0\cdot 000_7$	$2\cdot_8 \times 10^{-4}$	$0\cdot 0001_2$
	1,000	$2\cdot_0$	$+0\cdot 002_5$	11×10^{-4}	$0\cdot 0002_2$
	1,500	$4\cdot_5$	$+0\cdot 006$	25×10^{-4}	$0\cdot 0003_5$
	2,000	$8\cdot_1$	$+0\cdot 010$	45×10^{-4}	$0\cdot 0004_4$
5,000	500	$1\cdot_3$	$+0\cdot 002_6$	$2\cdot_6 \times 10^{-}$	$0\cdot 0001_3$
	1,000	$5\cdot_4$	$+0\cdot 007_0$	11×10^{-4}	$0\cdot 0002_2$
	1,500	$12\cdot_1$	$+0\cdot 017$	24×10^{-4}	$0\cdot 0003_6$
	2,000	$21\cdot_7$	$+0\cdot 033$	44×10^{-4}	$0\cdot 0005_2$
6,820	500	$1\cdot_7$	$+0\cdot 002_8$	$2\cdot_5 \times 10^{-4}$	$0\cdot 0001_3$
	1,000	7	$+0\cdot 011$	10×10^{-4}	$0\cdot 0002_5$
	1,500	15	$+0\cdot 026$	22×10^{-4}	$0\cdot 0004_1$
	2,000	28	$+0\cdot 048$	41×10^{-4}	$0\cdot 0005_6$
10,000	500	$2\cdot_5$	$+0\cdot 004$	$2\cdot_5 \times 10^{-4}$	$0\cdot 0001_3$
	1,000	$9\cdot_8$	$+0\cdot 016$	$9\cdot_8 \times 10^{-4}$	$0\cdot 0002_6$
	1,500	22	$+0\cdot 040$	22×10^{-4}	$0\cdot 0004_3$
	2,000	39	$+0\cdot 075$	39×10^{-4}	$0\cdot 0006_0$

TABLE VI.—*Frequency Corrections* 10mH *Campbell Inductometer* (*continued*).
Common point HC_2. Mutual inductance negative.

Instrument reading μH.	Frequency.	ΔM (μH)	σ (ohms).	$\frac{\Delta M}{M_0}$	$\frac{\sigma}{M\omega}$
1,820	500	$0\cdot_5$	$-0\cdot 000_7$	$2\cdot_5 \times 10^{-4}$	$0\cdot 0001_2$
	1,000	$2\cdot_0$	$- \cdot 002_6$	11×10^{-4}	$0\cdot 0002_3$
	1,500	$4\cdot_4$	$-0\cdot 006_7$	24×10^{-4}	$0\cdot 0003_9$
	2,000	$8\cdot_4$	$-0\cdot 013$	46×10^{-4}	$0\cdot 0005_7$
5,000	500	$1\cdot_2$	$-0\cdot 002_3$	$2\cdot_4 \times 10^{-4}$	$0\cdot 0001_4$
	1,000	$5\cdot_8$	$-0\cdot 010$	12×10^{-4}	$0\cdot 0003_2$
	1,500	$13\cdot_0$	$-0\cdot 026$	26×10^{-4}	$0\cdot 0005_5$
	2,000	$25\cdot_4$	$-0\cdot 050$	51×10^{-4}	$0\cdot 0008_0$
6,820	500	2	$-0\cdot 003_9$	$2\cdot_9 \times 10^{-4}$	$0\cdot 0001_8$
	1,000	9	$-0\cdot 017$	13×10^{-4}	$0\cdot 0004_0$
	1,500	20	$-0\cdot 041$	29×10^{-4}	$0\cdot 0006_3$
	2,000	36	$-0\cdot 080$	53×10^{-4}	$0\cdot 0009_3$
10,000	500	$3\cdot_8$	$-0\cdot 006_0$	$3\cdot_8 \times 10^{-4}$	$0\cdot 0001_9$
	1,000	15	$-0\cdot 028$	15×10^{-4}	$0\cdot 0004_5$
	1,500	35	$-0\cdot 067$	35×10^{-4}	$0\cdot 0007_0$
	2,000	62	$-0\cdot 134$	62×10^{-4}	$0\cdot 0010_7$

points are possible. The corrections were determined in each case for the reading M_0=10mH. The results are collected in Table VII.

TABLE VII.—*Frequency Corrections of Campbell Inductometer for Various Common Points.*
Instrument reading: 10mH. Frequency: 1,000∼.

Common point.	Sign of M.	$\frac{\Delta M}{M_0}$	σ	$\frac{\sigma}{M\omega}$
HA_0	+	$9{\cdot}_8 \times 10^{-4}$	+0·016	$0{\cdot}0002_6$
FC_2	+	$8{\cdot}_2 \times 10^{-4}$	+0·015	$0{\cdot}0002_4$
HC_2	−	$15{\cdot}_8 \times 10^{-4}$	−0·028	$0{\cdot}0004_5$
FA_0	−	$11{\cdot}_8 \times 10^{-4}$	−0·021	$0{\cdot}0003_3$

It is evident that it is important always to use a common point the corrections for which are known.

The values in Tables V, VI and VII all refer to the 10mH Campbell instrument, which is the most generally useful size of inductometer. The corrections for a 1mH instrument are somewhat smaller, since the capacity effects are naturally of less importance in coils of smaller self-inductance. Values for a 1mH instrument at the top of its scale are given in Table VIII. Here, again, the phase angle error is by no means negligible at 1,000 cycles.

TABLE VIII.—*Frequency Corrections of* 1mH *Mutual Inductance* (*Campbell type*).
Frequency: 1,000∼.

Common point.	Sign of M.	$\frac{\Delta M}{M_0}$	σ	$\frac{\sigma}{M\omega}$
HA_0	+	$1{\cdot}_9 \times 10^{-4}$	$+0{\cdot}001_5$	$0{\cdot}0002_4$
EC	+	$1{\cdot}_7 \times 10^{-4}$	$+0{\cdot}001_5$	$0{\cdot}0002_4$
EA_0	−	$2{\cdot}_4 \times 10^{-4}$	$-0{\cdot}001_7$	$0{\cdot}0002_7$
HC	−	$2{\cdot}_5 \times 10^{-4}$	$-0{\cdot}001_7$	$0{\cdot}0002_7$

In the case of the 100mH inductometer of the Campbell type the frequency corrections become much more serious. At 1,000∼ the correction on mutual inductance amounts to 1 per cent., and the phase defect is about 0·001. In fact, this instrument is not at all suitable for high-frequency work, and its properties have not therefore been examined in such detail. Actual values obtained for a 100mH Campbell inductometer are given in Table IX. Values of $\frac{\Delta M}{M_0}$ are given for a common point, making M positive, and also for one making it negative. When the instrument was used with the middle point of the primary connected to one point on the secondary (a convenient connexion for a self-inductance bridge), the frequency correction was found to be intermediate between those obtained for M positive and M negative respectively. The frequency coefficient $\frac{\Delta M}{M_0}$ was not approximately constant for different M_0 readings in the case of this instrument. For example, at the reading M_0=100mH, $\frac{\Delta M}{M_0}$ was about 1 per cent. at 1,000∼. At the reading M_0=50mH it amounted to 0·5 per cent., while for all readings below 10mH it was 0·3 per cent. At a given setting, M increased slightly more rapidly than the square of the frequency, but σ increased much more rapidly than the square of the frequency, as is evident from the values given in Table IX.

TABLE IX.—*Frequency Corrections of* 100mH *Campbell Inductometer.*

Common point.	Sign of M.	Frequency.	ΔM mH	σ (ohms).	$\frac{\Delta M.}{M_0}$	$\frac{\sigma}{M\omega}$
DE	+	500	0·24	$0{\cdot}08_2$	$0{\cdot}2_4\times10^{-2}$	$0{\cdot}0002_6$
		1,000	1·03	0·60	$1{\cdot}0_3\times10^{-2}$	$0{\cdot}0009_5$
		1,500	2·41	1·99	$2{\cdot}4_1\times10^{-2}$	0·0021
		2,000	4·79	4·6	$4{\cdot}7_9\times10^{-2}$	0·0035
DF	—	1,000	1·42	...	$1{\cdot}4_2\times10^{-2}$	...

EFFECT OF DIELECTRIC LOSSES ON THE FREQUENCY CORRECTIONS.

Consider the general case of a mutual inductor with a common point. Let $\xi\eta$ represent the resistance operators of the coils apart from capacity effects and the dielectric losses associated with them. Let their mutual operator be m. The capacity, dielectric loss, and leakage effects may be represented by shunts across the coils, whose conductance operators are α and β respectively, and the corresponding mutual effects (leakage and capacity) may be represented by a conductance (operator γ) across the open ends of the coils. Butterworth has shown that this system may be reduced by a series of transformations to the system of Fig. 3 in which we have two simple arms (resistance operators ξ' and η') with a mutual operator m', but no shunting conductances. When the terms, α, β, γ are small compared with ξ, η, m, which is the case in all mutual inductance standards at telephonic frequencies, the equivalent operators are given by the approximate equations

$$\left.\begin{aligned} m' &= m+\alpha(\xi-m)(\eta-m)-\beta m\eta-\gamma m\xi \\ \xi' &= \xi-\alpha(\xi-m)^2-\beta m^2-\gamma\xi^2 \\ \eta' &= \eta-\alpha(\eta-m)^2-\beta\eta^2-\gamma m^2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Considering the case of alternating currents of frequency $\frac{\omega}{2\pi}$ we may replace these operators by vector impedances or conductances. Let R_1, R_2 be the resistances of the coils L_1, L_2 M the inductances. The conductance terms α, β, γ must include self-capacity, leakage, and dielectric loss terms. Thus, we may write

$$\left.\begin{aligned} &\alpha=G_1+j\omega C_1 \qquad && \beta=G_2+j\omega C_2 \qquad && \gamma=G_3+j\omega C_3 \\ &\xi=R_1+j\omega L_1 && \eta=R_2+j\omega L_2 && m=j\omega M \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

We may also write

$$\left.\begin{aligned} m' &= \sigma+j\omega(M+\triangle M) \\ \xi' &= R_1+\triangle R_1+j\omega(L_1+\triangle L_1) \\ \eta' &= R_2+\triangle R_2+j\omega(L_2+\triangle L_2) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $\triangle M$, σ, $\triangle L$, etc., may be regarded as the effects of self-capacity, leakage, etc., on resistance, inductance, or impurity. Substituting (11) in (10), and then comparing the result with (12), we find

$$\begin{aligned} \triangle M=C_{12}R_1R_2+\omega^2\{L_1C_1M+L_2C_2M-C_{12}(L_1-M)(L_2-M)\}-R_1G_1M-R_2G_2M \\ +G_{12}\{R_2(L_1-M)+R_1(L_2-M)\} \quad . \quad . \quad . \quad (13) \end{aligned}$$

$$\sigma=\omega^2[C_1R_1M+C_2R_2M-C_{12}\{R_1(L_2-M)+R_2(L_1-M)\}]+G_1L_1M\omega^2+G_2L_2M\omega^2$$
$$-\omega^2G_{12}(L_1-M)(L_2-M)+G_{12}R_1R_2\,. \quad . \quad . \quad (14)$$
$$\triangle L_1=-(C_1+C_{12})R_1^2+\omega^2\{C_1L_1^2+C_2M^2+C_{12}(L_1-M)^2\}-2G_1L_1R_1$$
$$-2G_{12}R_1(L_1-M) \quad . \quad (15)$$
$$\triangle R_1=2\omega^2R_1\{C_1L_1+C_{12}(L_1-M)\}-(G_1+G_{12})R_1^2+\omega^2\{G_1L_1^2+G_2M^2$$
$$+G_{12}(L_1-M)^2\}. \quad . \quad . \quad . \quad (16)$$

Thus, the frequency coefficient $\frac{\triangle M}{M}$ involves capacity terms of the form $L_1C_1\omega^2$ and also conductance terms of the form G_1R_1. G_1 represents not only leakage such as would be measured by a direct current test, but also the dielectric losses. In a well-constructed coil the D.C. leakage is very small compared with the alternating-current conductance due to dielectric losses. If δ is the loss angle of the insulation then $\tan\delta_1=\frac{G_1}{C_1\omega}$. G_1 is usually small compared with $C_1\omega$ (e.g., $\tan\delta$ is not likely to exceed 0·05 in a good coil), and R_1 is usually small compared with $L_1\omega$. Thus terms such as G_1R_1 are small compared with those such as $L_1C_1\omega^2$, and, therefore $\triangle M$ will depend almost entirely on the capacity terms. Further, since C_1C_2, etc., are practically independent of the frequency, $\triangle M$ will be proportional to the square of the frequency. This fact is verified by the experimental results quoted above.

In the expression for σ the capacity terms are of the form $C_1R_1M\omega^2$, whilst the conductance terms are of the form $G_1L_1M\omega^2$. When the inductance L_1 is high, this term is by no means negligible compared with the capacity term. Also, since G_1 is not even approximately independent of the frequency, this term will not be proportional to the square of the frequency. In a well-constructed coil, the conductances G_1, G_2, etc., will be almost entirely due to dielectric absorption effects in the insulated covering of the wire forming the coils. The conductance due to such effects varies with frequency, at any rate over the telephonic range, in accordance with the formula*

$$G_1=G_0'\omega^a,$$

where G_0' is independent of frequency, and a is a constant, for a given material under definite conditions as to temperature, etc. In general, $0<a<1$. Thus, the conductance terms in σ are of the form $G'_0L_1M\omega^{2+a}$, and consequently σ increases more rapidly than the square of the frequency. This was found to be the case even for a 10mH inductometer, showing that dielectric loss effects were not negligible even in that case. In the case of the 100mH inductometer, it was evident that the observed σ was mainly due to conductance arising from dielectric losses since σ is approximately proportional to $\omega^{2.9}$. It is evident that the increase in effective resistance of the primary coil, $\triangle R_1$ will be similarly affected by conductance, while the effect on the change in effective inductance of the primary coil, $\triangle L_1$, will, like that on $\triangle M$, be very small.

THE BUTTERWORTH-TINSLEY INDUCTOMETER.

The sub-division of the dials in the Campbell type of inductometer is usually obtained by winding one coil with a cable of ten strands twisted together, putting the ten strands in series to form the reading 10 of the dial, and taking tappings from the junctions of the various strands to the studs 1, 2, 3, . . . etc. By this arrangement only one adjustment is necessary for each dial, and the accuracy of sub-division is of a very high order. This method of winding does, however, introduce large capacity effects into the coil in question, and the frequency errors are correspondingly large at high frequencies. Butterworth suggested that for work at high frequencies, a more perfect mutual inductance might be obtained by using for each dial, three mutual inductances with a common primary, the values being the 6, 3 and 1 of the dial in question. These three coils must be independently adjusted, but the other points on the dial are obtained by addition and subtraction of the three, e.g., 10 is given by 6+3+1, 9 by 6+3, 8 by 6+3 −1, and so on. It is, of course. necessary to devise a form of switch for connecting up the coils in the proper manner. The coils not required at any particular setting of the dial, are left isolated—e.g., at the setting 9, the 6 and 3 coils are connected in series, and the 1 coil is disconnected.

---

* See, for example, McLeod, Phys. Rev., Vol. XXI., p. 53 (1923) ; Granier, Bull. de la Soc. Francaise des Electriciens, Vol. III., p. 333 (1923).

The capacity effects in coils of this construction are much smaller than in the stranded cable coils, and thus the frequency corrections are correspondingly smaller. An inductometer constructed in this manner by the firm of Messrs. Tinsley & Co. was tested in the same way as the Campbell instrument previously referred to. The values obtained are given in Table X. The frequency corrections are seen to be of the order of one-third to one-seventh of the corresponding corrections in the Campbell instrument, and the new instrument has, therefore, considerable advantages for high-frequency work. The Campbell instrument has, however, important advantages for standardising work which can be carried out at low frequency. It was, of course, designed for such work since the accuracy of sub-division of the dials is usually greater, and the form of dial used readily lends itself to the calibration of each reading in terms of the maximum reading, without the aid of another standard.

TABLE X.—*Frequency Corrections of* 10 *mH Butterworth-Tinsley Inductometer.*

Common Point.	M reading.	Frequency. ∼ /sec.	ΔM (μH).	σ (ohm).	$\frac{\Delta M}{M}$	$\frac{\sigma}{M\omega}$
D.C.	$+5{,}000\,\mu H$	1,000	0·7	$0{\cdot}001_5$	$1{\cdot}_3\times10^{-4}$	$0{\cdot}_5\times10^{-4}$
		2,000	$2{\cdot}_6$	0·007	$5{\cdot}_2\times10^{-4}$	$1{\cdot}_1\times10^{-4}$
	$+10{,}000\,\mu H$	1,000	$1{\cdot}_3$	0·004	$1{\cdot}_3\times10^{-4}$	$0{\cdot}_6\times10^{-4}$
			$5{\cdot}_2$	0·015	$5{\cdot}_2\times10^{-4}$	$1{\cdot}_2\times10^{-4}$
D.B.	$-10{,}000\,\mu H$	1,000	$-3{\cdot}_1$	$-0{\cdot}008_7$	$3{\cdot}_1\times10^{-4}$	$1{\cdot}_3\times10^{-4}$
		2,000	−12	$-0{\cdot}004_4$	12×10^{-4}	$3{\cdot}_5\times10^{-4}$
		4,000	−51	−0·21	51×10^{-4}	$8{\cdot}_4\times10^{-4}$

It is evident that dielectric losses are also appreciable in this instrument, since σ (when *DB* is common) increases more rapidly than the square of the frequency.

In conclusion, I wish to express my thanks to Messrs. D. W. Martin and D. A. Oliver, of the Electrical Department, N.P.L., for assistance in taking some of the observations recorded in this Paper.

DISCUSSION.

Mr. A. CAMPBELL (communicated): I warmly congratulate Mr. Hartshorn on his success in solving the difficult problem of the measurement of small impurity in mutual inductances. He has skilfully got round the difficulty by working downwards from radio frequencies, which exaggerate the effects in question. Of the two methods of comparison used by the author, the one for equal inductances was introduced by me many years ago for the purpose of balancing the out-of-phase component, before " impurity of M " had been exactly defined, and it has proved useful even for extremely impure mutual inductances, such as iron-cored current transformers. Some time after my publication of the method (N.P.L. Report for 1908), Professor A. Larsen, of Copenhagen, extended it, and made it the basis of his beautifully simple alternating-current potentiometer. It is interesting to notice that, if the detecting instrument and the current source are interchanged it becomes Mr. Dye's method of testing voltage transformers.

The comparison of unequal mutual inductances is a good deal more difficult ; Mr. Hartshorn's new method for this is excellent, and, being a great advance on the older methods, it should be regarded as the standard procedure. The author's results will afford the users of strand-subdivided inductometers suitable corrections where these are required ; it should be remembered, however, that it is only in rather extreme cases (such as for the power losses in very perfect condensers or in very highly inductive coils) that the errors are of much consequence. As a means of obtaining quick and accurate subdivision of mutual inductances the stranding system still holds its own, having been for many years the key to the easy dissemination of very accurately subdivided standards. Of late years I have constructed inductometers by other more laborious systems, and I trust that when one of the new type passes through the author's hands it will be found fairly free from impurity errors.

AUTHOR'S reply : I am grateful to Mr. Campbell for his kind appreciation of my Paper. I was unaware of the exact history of the method for comparing equal mutual inductances, although I knew that Mr. Campbell's Papers treat the properties of the " MR element " very thoroughly and that he had used it in a variety of measurements some years ago. I shall look forward with interest to the appearance of his new inductometer.

XXXI.—A NOTE ON λ4722 OF BISMUTH AND THE NATURE OF " RAIES ULTIMES."

By A. L. Narayan and K. R. Rao.

Received March **3, 1926.**

Abstract.

Following the previous experiments of one of the authors on the nature of the green line λ5350 of thallium, a detailed examination of λ4722 of bismuth was made with a quartz Lummer plate, and it has been found that there is not even the slightest trace of absorption in the main component or in the satellites, even at 1,000° C. The fluorescence of the vapour under optical stimulation was studied, and it was found that when excited by radiation of wavelength from λ6000 to 3500 the fluorescence was a banded spectrum in the orange-yellow, while when excited by ultra-violet radiation from a bismuth arc, the fluorescence was bluish, and consisted of λλ4722 and 3068, thereby showing that λ3068 represents the minimum excitation energy and corresponds to transition to the normal orbit.

A NUMBER of investigators have called attention to the great intensity of the line λ4722 in the emission spectrum of bismuth vapour. Foote and Mohler have recorded this as a " raie ultime " and resonance line. According to de Gramont also, the line λ4722 constitutes the " raie ultime." Generally, the raies ultimes are supposed to be the resonance lines and the first members of principal series. They therefore correspond to transitions to the lowest level of the atom, and should be absorbed by the non-luminous vapour of the metal. In the course of our experiments on the absorption of bismuth vapour it was found that the line was not absorbed by a column of the non-luminous vapour even at the highest temperature used, viz., 1,400° C. So far as the authors are aware, no investigator has recorded the absorption of this line. Experiments recently conducted in this laboratory on the structure and absorption of the green line λ5350 of thallium and published in the Proc. Roy. Soc., showed that this line was complex, and that at about 800° C. only the main component was absorbed, while the absorption of satellites commenced at higher temperatures. It was therefore thought that possibly in the case of λ4722 of bismuth a similar thing might happen.

In this connexion it will be remembered that numerous physicists have studied in recent years the structure of this radiation, notable among them being Gehrcke and Bayer, Takamine, Aronberg and Nagaoka and Suguira, and have called attention to the great complexity of this line.

With a view, therefore, to determine whether this line actually represents the transition to the normal state of the atom, it was decided to study at length the absorption of this line with instruments of high resolving power. Detailed examination of the absorption of this line was made by a quartz Lummer-Gehrcke plate of resolving power equal to 300,000, as a result of which it was found that even at 1,200° C. there was not the slightest absorption, either in the main component or the satellites, as is clear from Fig. 1.

In these experiments radiation from a vacuum arc lamp, the lower electrode of which was a carbon cup containing bismuth which the upper electrode was pure carbon, was examined by the L.G. plate before and after passing through a long column of bismuth vapour. Fig. 1 (*a* and *b*) are the Lummer patterns of this line before and after passage through the vapour at about 1,000° C.

In recent years Klein and Rosseland* have shown from thermo-dynamic considerations that by impacts of activated atoms with electrons, atoms and molecules, transformations can take place unaccompanied by radiation. Franck and Cario† have shown that this active energy may be related to a variety of energetic exchanges, and that the argument of Klein and Rosseland could be used to prove the reversibility of excitation by atomic impacts. This showed that excited Hg atoms colliding with neutral atoms of a vapour that does not absorb the effective radiation may excite the atoms of the vapour, causing them to emit fluorescence spectra, provided the excitation potential of the vapour is less than 4·9 volts (the energy equivalent of $\lambda 2536$). Such activated fluorescence was used in recent years by Franck and Cario, Kofferman‡ and Donat§ for testing series relationships. Kofferman found that in the case of bismuth the lines $\lambda\lambda 4722$ and 3068 were excited. In the experiments of these authors, as energy was communicated to the atoms of the gas in question by excited Hg atoms, it was not possible for them to find the minimum amount of energy required to excite the atom of the gas in question, and thus obtain information regarding the ground orbit of the atom. Experiments were therefore made by the authors to study the fluorescence of bismuth vapour when excited by different monochromatic radiation.

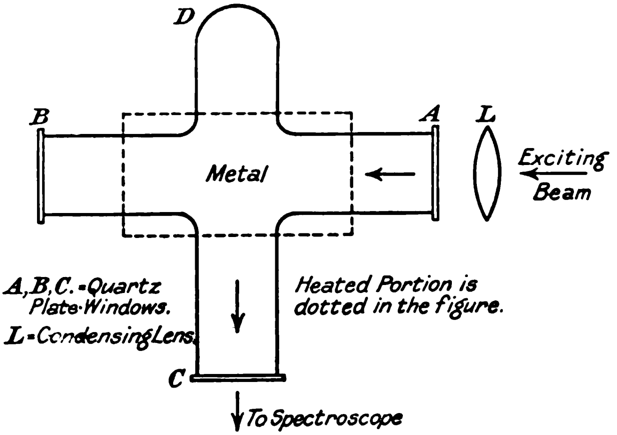

D
B
A
L
Metal
Exciting
Beam
A,B,C.-Quartz Plate-Windows.
L-Condensing Lens.
Heated Portion is dotted in the figure.
C
To Spectroscope

FIG. 4.

The vessel used for these experiments was in the form of a cross and made of seamless steel tubing 1 in. in diameter, having welded joints at the cross. A diagrammatic sketch of the apparatus is given in Fig. 4. The end D is permanently closed with a welded joint so as to serve as a perfectly dark background.

The primary or exciting beam passes along AB, and is brought to a focus at the centre of the cross, and fluorescence was observed in the direction DC against the

---

* Klein and Rosseland, Zeit. f. Phys., 4, 46 (1921).

† Franck and Cario, Zeit. f. Phys., 10, 185 (1922).

‡ Kofferman, Zeit. f. Phys., 21, 316 (1924).

§ K. Donat, Zeit. f. Phys., 19, 345 (1924).

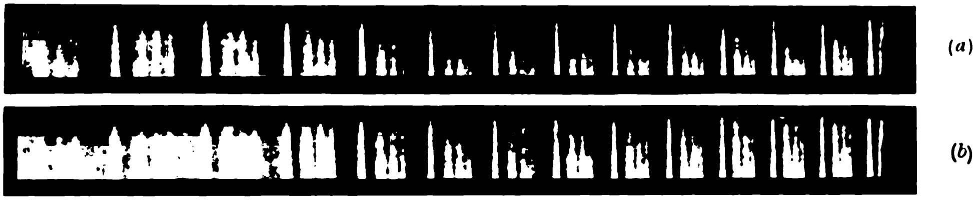


FIG. 1.

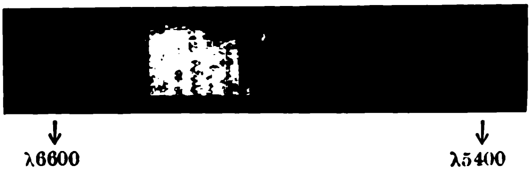


FIG. 2

FIG. 3.

To face page 322]

UNIV. OF MICH.

black background. With a view to photograph even the faint fluorescent light, it became necessary to avoid all scattered light, and therefore between the slit of the observing spectrograph and the end C of the cross there were placed a number of co-axial diaphragms. The dotted portion was subjected to preliminary heating, and the tube was exhausted to a pressure of 1 mm. at 200° C., and then the temperature was raised to 550-600° C., when observations were made in the lateral direction by illuminating the vapour with different radiations, obtained by using different colour filters.

When excited by radiation of different wavelengths from $\lambda 6000$ to $\lambda 3500$, the fluorescence consisted of a banded emission, Fig. 2, in the orange-yellow, exactly corresponding to the banded spectrum emitted by the vapour under purely thermal excitation at about 1,300° to 1,400° C. recently photographed by one of the authors, the only difference between these two being that in temperature emission the bands are sharp. But when the vapour was excited by light from the bismuth arc, in which the radiation $\lambda 3068$ was predominant, it was found that the fluorescent radiation was bluish, which was found to correspond to $\lambda 4722$ and 3068; and, further, when the ultra-violet radiation from the arc was cut off by the interposition of a glass plate, the bluish fluorescence was suddenly extinguished, thereby showing clearly that $\lambda 3068$ corresponds to the minimum excitation energy of the vapour and that this line corresponds to the transition of the valence electron to the normal orbit of the atom, while $\lambda 4722$ corresponds to transition to an excited state. Further, in spite of the fact that the probability of transition to the normal orbit is necessarily greater than that to the excited state, and that, therefore, $\lambda 3068$ should be more intense, this line is observed to be weaker than $\lambda 4722$ in Fig. 3. This is probably due to the fact that $\lambda 3068$ is reduced in intensity on account of absorption by the cooler vapour in the surrounding region.

These observations, together with those on the absorption of $\lambda 4722$, clearly show that $\lambda 4722$ corresponds to a transition to one of the excited states.

XXXII.—THE DISTRIBUTION OF INTENSITY IN A POSITIVE RAY SPECTRAL LINE.

By M. C. Johnson, *M.A.*, *M.Sc.*, Birmingham.

Received March 6, 1926.

(*Communicated by* Prof. S. W. J. Smith.)

Abstract.

In studying the intensity distribution in a spectral line emitted by positive rays, a line structure was found which is not familiar in ordinary discharge tube spectra. This structure would not appear under the low resolving powers necessitated by the extreme faintness of the light emitted in most investigations of Stark and Doppler effects in positive rays. The technique required to make possible the study of structure in such faint lines is discussed in detail. The explanation of the structure in terms of Doppler and Stark components is compared with the theory of broadened lines in ordinary discharge tube spectra.

Introduction.

The work of Wien and his pupils* has shown that when positive rays have passed through a perforated cathode the conditions under which they excite spectra are more simple and controllable than the spectral conditions of an ordinary discharge tube. On this account the spectroscopy of positive rays has been exhaustively studied by Stark, Wien and others for the splitting of lines in applied homogeneous electric fields, and for the shift of lines due to the comparatively homogeneous velocities of the ions in the positive ray stream. This work has, however, mostly been carried out with prismatic spectrographs. The present Paper describes an attempt to apply to positive rays the more minute examination of interference analysis, aided by the wedge method of studying intensity distributions in spectral lines, due to Merton. To eliminate the large Stark effects studied by other workers, the positive rays were allowed to stream into a chamber which was either made electrically force-free or could be subjected to small known potential differences. To eliminate large Doppler effects, the positive ray chamber was made narrow enough to act itself as a wide slit source of light, and the collimating axis of the optical train was kept perpendicular to the axis of the discharge tube.

I.

The light emitted in the positive ray chamber is very faint compared with usual sources of illumination in spectroscopy. The prismatic photographs of previous workers have required exposures of several hours. To attempt further a study of intensity distribution across a highly resolved line structure requires a combination to be made of several optimum conditions. Some of these conditions involve problems about which evidence is conflicting or uncertain. We shall discuss the following :—

---

* Summarised in Handbuch der Radiologie, IV, 1 (1923). *See* also Proc. Phys. Soc., 37, 324 (1925).

(1). The design of tube and cathode to provide the greatest intensity of positive ray light.

(2). The control of the intensity ratio of the required lines to other associated spectra.

(3). The thermal and mechanical stability of the system for long exposures.

(4). The photographic sensitivity of plates for definite spectral regions.

(5). Use of the wedge and measurements required with it.

(1). Each of the successive discharge tubes used was made up of two pieces of glass tubing, about 30 cm. and 5 cm. long respectively, waxed on to opposite sides of a central disc which held the cathode, and which could be water cooled (Fig. 1).

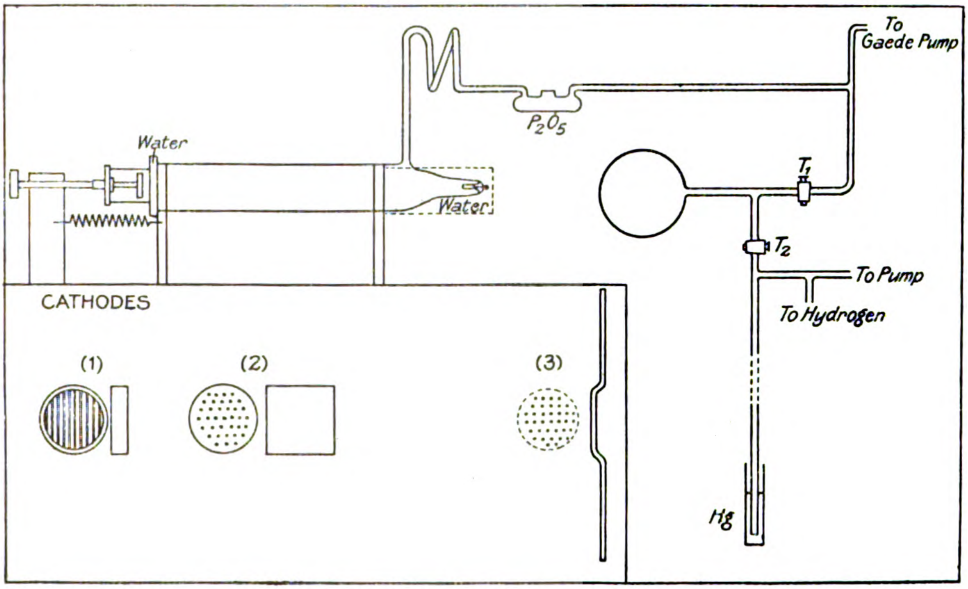


FIG. 1.

This general type of design was taken from the Shearer X-ray tube, and is an exception to the remark of Wien[*] that in England a spherical positive ray chamber is the rule. It has the advantage of allowing several cathodes in turn to be inserted in the central disc, and also of allowing a rigid auxiliary electrode to slide in and out of the brass end piece of the chamber furthest from the anode. The anode end was drawn off into a narrow tube for its electrode, as this causes the tube to be self-rectifying.[†] It was soon found that the diameter of the perforated cathode need not be much greater than 1·5 cm., as when the gas pressure is low enough to allow positive rays to develop, the stream becomes concentrated along the axis of the tube.

The thickness of the cathode and the size of perforations was found to be very important. Under many conditions a beam of positive rays in hydrogen extends luminous for several centimetres, until the pressure is below 0·03 mm. Hg.* Relying on this, one cathode (Fig. 1, inset 2) was made nearly 2 cm. thick, to enable the light behind to be observed clear of the central disc of the tube. The cathode, however, only allowed very faint luminosity in the positive ray chamber. A much thinner cathode was built up of aluminium blocks, separated at their ends by aluminium strips 0·1 mm. thick (Fig. 1, inset 1). This gave a greater intensity of positive ray light, in spite of the very narrow apertures. Since this increased intensity seemed traceable to decrease of thickness of cathode rather than to increase of perforation aperture, which was negligible, a final cathode was made as follows: A sheet of aluminium 3/32 in. thick was cut into a disc about 10 cm. diameter, and spun in a lathe while a blunt tool pressed out the central two centimetres. As many 1 mm. holes as possible were then drilled in this central portion. The two glass tubes were waxed on to opposite sides of this disc, the central portion projecting sufficiently (Fig. 1, inset 3) to allow a small angle of illumination to emerge from the positive ray chamber, and yet not projecting enough to encourage the positive rays in the main tube to diverge to the non-perforated edge of the disc. The parallelism of the back of the cathode with the auxiliary electrode was secured by accurate grinding of the edges of the shorter glass tube.

---

[*] Proc. Phys. Soc., 37, 332,

[†] Aston, Isotopes, 48,

With this final form of tube, at 3 milliamps. discharge current, the positive ray glow between cathode and auxiliary electrode was a brilliant and perfectly homogeneous disc of light, 1·5 cm. diameter and 0·14 cm. thick, as bright as any part of the discharge tube. With hydrogen, its visual intensity rose as the gas pressure in the whole tube was decreased, had a maximum corresponding to a dark space of about 5 cm., and at still lower pressures became fainter.

(2). Hydrogen in a discharge tube can emit a many-lined spectrum and a continuous spectrum, as well as the Balmer series, with whose lines we are concerned. It is therefore necessary, in any work where economy of light is urgent, to investigate the control of the ratio of intensities in these spectra.

Since the many-lined spectrum is molecular and the Balmer spectrum atomic, some means must be found of suppressing the recombination of dissociated molecules. Alternatively, we must increase the exciting agency to allow predominance of those encounters which not only dissociate but ionise. According to R. W. Wood† and Merton,‡ water vapour brings out the Balmer series sharply, probably through the former alternative, by suppressing the catalysis of the glass surface. R. W. Wood increases excitation by the high current densities of a condensed discharge, which he finds improves the Balmer spectrum. This was tried in the present experiment, but condensers in the circuit decreased the intensity of the positive rays, and slightly decreased the ratio of the Balmer intensity to the many-lined intensity. This is one of the many cases in which positive ray luminosity does not follow the same law as the ordinary discharge. The low gas pressures required for positive rays prohibited the use of water vapour to intensify the Balmer spectrum. G. P. Thomson states§ that in the positive ray spectrum of hydrogen the atomic lines are strongest relative to the molecular lines at the higher pressures; but his pressures are all very

---

[*] Dempster, Astroph. J., 57, 193 (1923).

[†] Phil. Mag., 42, 729 (1921), and 44, 538 (1922).

[‡] Proc. Roy. Soc., A., 97, 307 (1920).

[§] Phil. Mag., 40, 240 (1920).

much lower than those in Wood's and Merton's ordinary tube spectra, where water vapour was successfully employed. Stark* insists on great purity of the gas for the strength of Balmer lines in positive rays. Having found the weakness of the analogy between ordinary spectra and positive ray spectra, this insistence was followed rather than the reliance on impurities advised by Wood and Merton. In the present work the hydrogen was taken from a commercial cylinder, and freedom from intermixture with air was secured by the following means (Fig. 1) :—

The tap T_2 is closed and T_1 opened, while the whole system is evacuated to a cathode ray stage in air. T_1 is then closed. The lower tubes are then evacuated until mercury is high in the long vertical tube. Gas is then admitted until it drives the mercury down again, and bubbles out in the bottom vessel. This tube is then re-evacuated and hydrogen again admitted. This is done several times, until the atmospheric impurities in the hydrogen below T_2 must be extremely slight. T_2 is then opened, and the spherical reservoir filled at atmospheric pressure. T_2 is then closed, and the reservoir suffices for repeated washing out of the whole apparatus with hydrogen, and for several weeks' refillings of the discharge tube. Observations can then be made with always the same degree of gas purity.

Each time the apparatus was opened and air admitted during changes of cathode adjustment, etc., several days of repeated evacuation and washing out were required, owing to the large metal surfaces in the discharge tube, which required very extended treatment before they ceased to emit occluded gases under a heavy discharge. Stark's requirement of gas purity was confirmed, contrary to the experience with ordinary discharge tubes, the Balmer spectrum being very sensitive to the state of the metallic electrodes. If fresh hydrogen was admitted from the reservoir at any time, the intensity of the Balmer series did not at once increase, but only after an hour or two of discharge.

The relative intensity of Balmer to many-lined spectrum was examined throughout the tube at its best—i.e., when the apparatus had been sealed for some weeks. The ratio of these intensities was at its minimum near the anode, increased regularly along the tube up to the cathode face, and then suddenly increased again on the further side of the cathode. This observation is not in agreement with the common statement that the spectrum of the positive rays is the same as that of the cathode face.

The greatest intensity of the Balmer series was only reached after the apparatus had been sealed long enough for a film of sputtered metal to have covered the inside of the main tube. This probably acted as the water vapour is said to act in R. W. Wood's tubes—i.e., hindered the catalytic action of the glass in turning atomic hydrogen back into molecular, after dissociation in the discharge.

(3). Even with the maximum efficiency for the development of the Balmer lines by the above methods, the light in the positive ray chamber was far fainter than is usually accepted as a minimum for interferometer analysis. Exact focussing could only be done indirectly by illuminating the positive ray chamber from a brilliant external source of hydrogen radiation. Hence it was only possible by trial and error to ensure that the very narrow image of the chamber remained on the slit of the spectroscope during an exposure of several hours. The thermal and mechanical stability for this purpose of spectroscopes, wedge and camera were assured by building the apparatus up on stone piers, in an underground room with thick walls and no windows. The thermostatic properties of this room were tested to within 0·2°C. during the whole of the day. Night constancy was not so strictly guaranteed, and trouble invariably followed attempts to expose intermittently over more than a day.

---

* Ann. der Ph., 21, 401 (1906).

The stability of the tube itself was attained by fixing the cathode disc rigidly, and allowing expansion to take place in other directions which did not matter. The ebonite support of the cathode disc (Fig. 1) was rigidly fixed to the tube, and was itself held by a strong spiral spring to a very massive iron pillar attached to a slate slab. A fine screw adjustment pressed through an insulator against the small end of the discharge tube; focussing could be corrected by small movements of this screw, which then kept the cathode region fixed for a number of hours. The warming of the tube, which even water cooling of anode and cathode did not quite prevent, could then be neglected as a source of movement.

(4). Authorities differ as to the colour sensitivity of photographic plates. The researches of the American Bureau of Standards* indicate that most panchromatic plates allow as great a darkening, for equal conditions, in the H_β region as in the H_α region; but personal opinions of several workers place the H_β region sensitivity low. In the present case the intensity distribution in the Balmer series of the positive rays was such that, visually, H_β was clear through prismatic spectroscope and an échelon in series, but not through the wedge. H_α was not seen at all. But photographs on Ilford's special rapid panchromatic plates showed a much stronger H_α than H_β. Accordingly, most of the measurements had to be confined to H_α. For this line, exposures were reduced by bathing the plates for four minutes in a solution of 1 c.c. ammonia in 100 c.c. water, then washing in alcohol, drying, and exposing as soon as quite dry and firm. This treatment, based on the work of the Bureau of Standards, was found to produce at best several hundred per cent. increase of sensitivity to H_α, but hardly any increase for H_β. Occasionally the treatment, though applied without any change of procedure, failed, and decreased the sensitivity. Another peculiarity noticed was that darkening of the image increased with time of exposure up to about four hours, but beyond that did not increase. The known non-linear relation of darkening to time does not seem adequate to explain this, considering the faintness of light and image.

(5). The light entering the slit of the optical train passed through a Hilger constant deviation prism spectroscope, by which one wavelength was focussed on the slit of a twenty-plate échelon grating. A camera was improvised for this, taking small plates for a single spectral line. In front of the slit of the prism spectroscope was a wedge, of the type used by Merton.† It consists of a wedge-shaped piece of neutral tinted glass, 7 mm. high, cemented to a wedge of clear glass, the whole forming a parallel sided plate whose optical density varies from 0·2 at the bottom to 4·2 at the top. A spectral line seen through this wedge under high resolving power appears broad at the bottom, where not only the bright core, but the faint wings of the line, are transmitted, and narrows upwards until the increasing density of the wedge absorbs, firstly, wings and finally the core of the line. From measurements of apparent widths at different heights in the line, the intensity distribution across different forms of the same line radiation can be compared. For this measurement several instruments were used, a choice of magnifying powers being needed to bring out different features. A Hilger photo-measuring micrometer was compared with a Watson micrometer and microscope, fitted with an accurate two dimensional travelling stage. A Poynting parallel plate micrometer was also used for certain measurements.

---

* Scientific Papers, No. 422.

† Proc. Roy. Soc., A., 92, 322 (1916).

Owing to the curvature of all lines from a prismatic spectroscope, even illumination in the échelon image could only be obtained by careful adjustment of the relative apertures of the two slits. This had to be at the expense of the illumination of the lowest end of the wedge. Accordingly, all spectral lines had to be measured from the broadest part of the line upwards, and the falling off of intensity at the bottom of the line neglected.

II.

Photographs of H_α of the positive rays through prism and échelon showed always a broadened line. This was at first put down to movement, mechanical or thermal, during the long exposures with the earlier design of cathode, which sometimes amounted to nine hours. The precautions described in I(3) were adopted to eliminate this possibility. The broadening persisted, however, and it was not till the wedge was used that a definite reason for it could be assigned. To test the possibility of broadening being an instrumental defect not remedied by these arrangements, photographs were taken with very long exposures, but lower resolving power. The sharpness and fineness of the results showed that if a radiation was nearly monochromatic there was nothing in the apparatus to prevent it appearing so on the plate. This test also eliminated the possibility of the broadening being due to some unknown type of spreading of the image, affecting faint lines long exposed.

The broadening was thus accepted as characteristic of the positive ray light under high resolving power, and compared with the broadening of a line in ordinary tube spectra. Condensed discharges and uncondensed discharges were photographed with the échelon and wedge under the same conditions as the positive ray photographs. This was ensured by allowing them to illuminate the positive ray chamber itself from behind, and photographing the spectrum of the chamber with the same adjustments as when it was filled with the positive ray glow. Fig. 2 shows the exact intensity distribution across each line, measured by the methods described in I(5). The inset is a drawing of the general appearance of the three types of line. The ordinary tube spectra have widths in each case fading perfectly regularly from bottom to top of the wedge, that of the condensed discharge (*C*) obeying the law of that type of intensity distribution, and the uncondensed discharge (*B*) obeying its law; though in this case the difference between the two types is not large, as the condensed broadening had to be slight enough not to overpass the order separation of the échelon. The positive ray line (*A*), on the other hand, consists of a short dark region, representing a line almost as broad as that of the uncondensed discharge, but of only a small fraction of the latter's intensity, and hence broadened on a far more extensive scale. In contrast to this squat image is a faint central line, extending about three times the length of the former. This is very clear in all the negatives, but even in the best prints is hardly visible, on account of its faintness and fineness. Its different origin and constitution from that of the short broad line appears very strikingly under the microscopes, where high magnification causes it to disappear, leaving the whole image constituted by the broad portion alone.

III.

The measurements of Fig. 2 were calibrated by measuring the separation of orders in the échelon spectrum, the constants of which were calculated in a previous Paper.* The positive ray line has an apparent width of just over 0·5 A.U. at the base of the wedge. The possible reasons for the broadening of a line are as follows :—

(*a*) The random Stark effect of the intermolecular fields. This produces a symmetrical broadening in a line, such as those of hydrogen, whose Stark components are symmetrical. It occurs at high pressures or in condensed discharges, and is seen in its incipient stage in Fig. (*C*2). The continuous intensity curve is due to the random directions and magnitudes of the intermolecular fields. It is clear

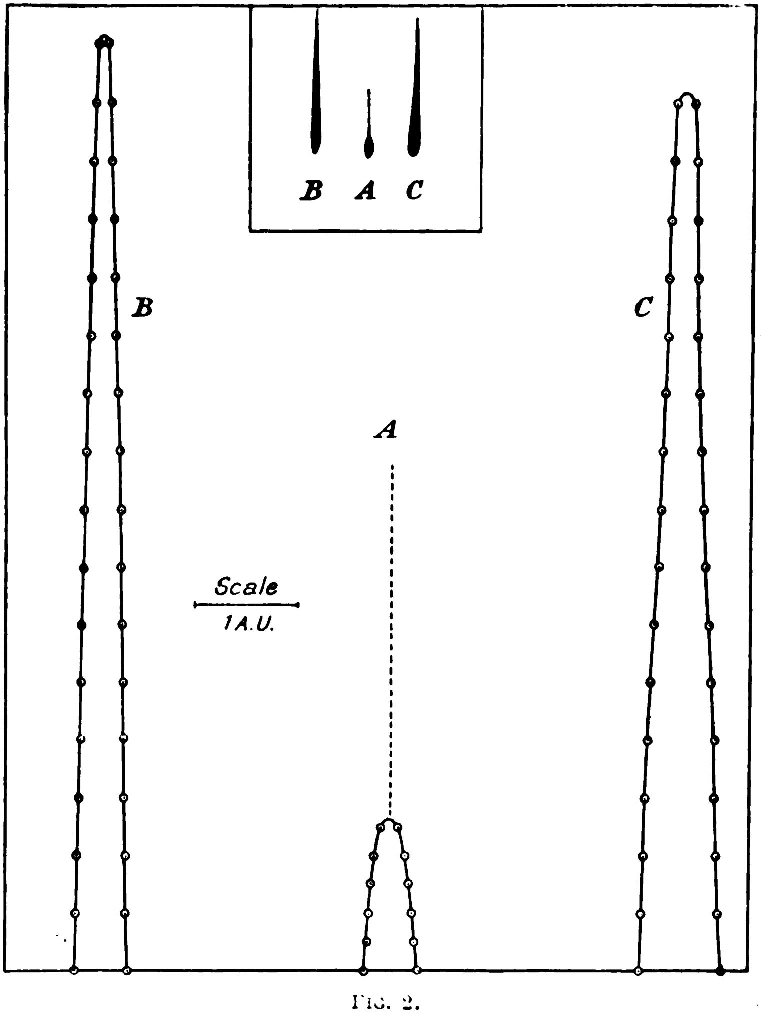


Fig. 2.

---

* Proc. Phys. Soc., 37, 249 (1925).

that this cannot account for the positive ray line, whose amount of broadening relative to central intensity is so much greater as to imply, on such an explanation, a density of charged atoms of a different order from any met with in these experiments. Nor would it account for the distinction of the short broad portion from the central line in the wedge image.

(*b*) The random Doppler effect due to the velocity of thermal agitation produces a broadening proportional to the square root of the temperature. That this is not the cause of the positive ray broadened line is clear from the fact that the positive ray chamber remained throughout very much cooler than the tube used for the uncondensed discharge, in which the random Doppler effect is the main source of breadth.

(*c*) In the positive ray chamber the direct Stark effect due to a unidirectional applied field would produce a broadening, if not sufficient to split the line into visibly separated components. To avoid the possibility of any such difference of potential being maintained between the cathode and auxiliary electrode, due to the latter charging up in some way, the two were in metallic connexion throughout these photographs.

(*d*) There remains the possibility of the broadening being due to a unidirectional Doppler effect—i.e., to the velocity of the ions moving towards the cathode in the potential fall of the dark space, and continuing their flight behind the cathode. Velocities up to 10^8 cm. per sec. have been observed in the positive rays when the slit of the spectroscope has been along the axis of the tube. To avoid these effects in the present case, when fine lines were desired, the axis of the optical train was perpendicular to the line of motion of the ions. It is possible, however,* that the slight unavoidable component of positive ion velocity allowed by the divergence of the beam from the chamber would be sufficient to account for the broadening.

The velocity v of a particle emitting light is related to the Doppler change of wavelength and the velocity of light c by the equation

$$d\lambda=\lambda\frac{v}{c}$$

while the velocity of the positive rays is related to the charge e and the mass m of the positive ion, and the potential V through which it has fallen in the dark space by the equation

$$v=\sqrt{\frac{2e}{m}V}$$

Now Wilsar has shown† that the Doppler shift of the spectral line from positive rays in certain gases does not increase indefinitely with the potential, but reaches a limit for a potential characteristic of the gas. This highest "effective" potential in hydrogen for producing Doppler effects is about 4,600 volts. Owing to the uncertainty as to whether all, or only the greater part, of the fall of potential across the discharge tube occurs in the dark space, it is not possible to know the exact potential through which the positive ions have fallen in the present case. It is certainly more than 4,600 volts. Since the charge and mass of the hydrogen positive ion are known, it can be shown from the above equations that to reduce the displacement for the maximum effective fall of potential in hydrogen, to the half width of the line observed in the present photographs, and interpreted as a Doppler effect, would require a numerical factor of about 70. This reduction would be effected by the sine of an angle of about 50′. If, then, some of the light which enters the slit of the spectroscope emerges from the positive ray chamber one degree on each side of the normal to the axis of the discharge tube, there will be a sufficiently large component of the velocity of the positive rays to produce a Doppler effect in the spectrum of the magnitude of the broadening measured. Even with a small aperture lens system, and the very narrow positive ray chamber used, this divergence must be reached. This explanation accounts for the symmetry of the broadening, since the divergence of the light introduces components both with and against the stream.

---

* I am indebted to a conversation with Mr. P. M. S. Blackett for this suggestion.

† Ann. der Ph., 39, 1251 (1912).

The explanation also accounts as follows for the faint " tail " seen in all the positive ray photographs. The positive ray chamber is known to produce two spectral lines in general for each monochromatic radiation, a line displaced by the Doppler effect, and an undisplaced line (Stark's " resting spectrum "). Wilsar showed* that the carriers of the displaced lines are the high velocity particles themselves, which come from the discharge tube and are stimulated to emit light by collisions with the gas in the positive ray chamber. Dempster† showed that the displaced spectrum is in some cases due to particles whose duration of luminosity has lasted during their flight since they became stimulated in the discharge tube itself. In both these cases, if photographs are taken along the axis of the tube, the Doppler effect is shown at its maximum, and the line appears to the violet side of its normal position. The " resting spectrum," on the other hand, is not subject to a Doppler effect, since it is emitted by the comparatively stationary atoms, which were already in the positive ray chamber, and are stimulated by the impact of the arriving positive ions.

The short and broadened part of the positive ray line in Fig. 2 is thus most probably due to small components in both directions of the moving spectrum, and the " tail," or central undisplaced line, is due to the " resting spectrum."

IV.

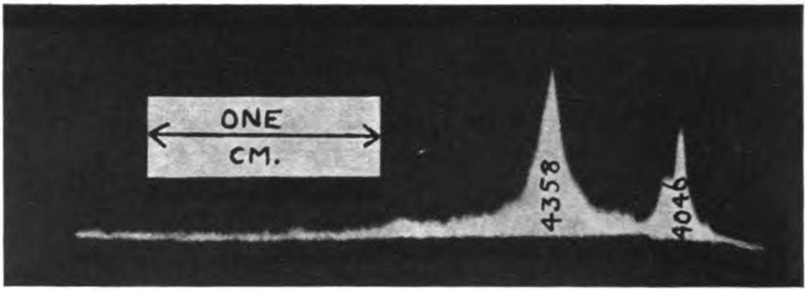
For comparison with the above results, small known potentials were applied between the cathode and auxiliary electrode, to find whether direct Stark effects could be detected superposed on the Doppler structure. For H_α no effect was detected with the small fields which could be maintained across the gap, whose conductivity could not be decreased without decreasing its luminosity. For H_β the displacement of Stark components is known to be greater than for H_α, and a direct Stark effect was less difficult to produce and measure. Unfortunately, the special hypersensitising methods described in I(4) are not applicable to the H_β region, and, even with the longest exposures, no satisfactory photographs were obtained through the Merton wedge. A plate of H_β, taken with échelon but without wedge, was measured. This contained two images, one taken with cathode and auxiliary electrode connected together, and one with a field of 1,700 volts per cm. applied

---

* Phys. Zeitshr., 12, 1091 (1911).

† Astroph. J., 57, 193 (1923).

UNIV. OF MICH.



"Edgewise" Spectral Photograph.

[*To face page* **333**

between them from a battery of accumulators. To eliminate the difficulty of even illumination caused by the curvature of the prismatic image, a corresponding point on each line was selected. The apparent widths, in the arbitrary units of the Hilger measuring instrument, were as follows :—

Without field: 17·4 16·5 17·1.
With field: 22·4 22·9 22·1.

In the arbitrary units of a Poynting parallel plate micrometer, the widths were found to be :—

Without field: 74 75 78.
With field: 109 111 109.

The ratio of the mean widths, with the two measuring instruments, was 1·3 and 1·4 respectively.

Owing to the uncertainties attendant on measuring apparent widths of lines—i.e., on measuring widths without knowing the intensity distribution—the results cannot be used in the problem of deciding the absolute value of the Stark displacements in very small fields. They are of interest as involving probably the smallest potential at which a Stark effect has been seen, and as comparing, in the same highly resolved spectrum, the orders of magnitude of direct Stark and Doppler effects, due to homogeneous fields and homogeneous velocities. Both these effects are only observable in positive ray spectra, and may be contrasted with the familiar indirect, or random, Stark and Doppler effects due to molecular fields and molecular agitation respectively, which determine the breadth of ordinary tube spectra.

It is a pleasure to thank Prof. S. W. J. Smith, F.R.S., for his kindly encouragement, and for the generous facilities he has provided for this work. I also owe a very great deal of instrument construction and help to Mr. G. O. Harrison.

DISCUSSION.

Mr. J. GUILD : There is just one practical point in connection with the wedge-method of spectrophotometry to which I would like to drawn the author's attention. It is probably not of serious consequence in work which is of a semi-qualitative character, but is of great importance if any attempt is made to derive accurate intensity information from wedge photographs. In most spectrographs the length of the slit is a fairly large proportion of the height of the various stops—diaphragms, prism boundary, etc.—which limit the pencil of rays reaching any part of the plate. In a Paper at the recent Optical Convention dealing with colorimetry and including spectrophotometry, I pointed out how serious errors may arise due to this fact. The difficulty could be avoided by using a specially designed instrument, or by inserting suitable stops in appropriate positions in existing instruments. Unless precautions of this character are taken, however, very large errors may be obtained.

Dr. L. F. RICHARDSON said that the difficulty mentioned by Mr. Guild might perhaps be overcome by omitting the grey wedge and placing the photographic film so that the light moved parallel to the plane of the film and struck one edge of the film nearly at right angles, the edge of the film passing through the centre of each of the spectral images of the slit. He had recently taken such an " edgeways " photograph of the bright spectrum of mercury vapour and had found that the relative photographic effects of the different spectral lines were very clearly shown : (i) By the relative depths to which light penetrated the film amounting to 1·5 cm. for the line 4358 Å ; and (ii) by the relative widths of the broadening, due probably to halation, near the edge where the light entered. To protect the broad faces of the film they were covered with black paper. To keep the film in a plane during exposure it was pressed between slabs of plate glass. The figure shows the result, except for much detail lost in reproduction. The exposure was 25 minutes. Ilford " double-coated X-ray film " was used. The rim of the lens which focussed the light, subtended an angle of 0·12 radian at the edge of the film, which was placed 0·4 cm. nearer the lens than the focal plane in air.

AUTHOR'S reply: With regard to Prof. O. W. Richardson's suggestion of comparing the shape of the undisplaced line in the longitudinal effect with the transverse spectrum, the échelon measurements of the latter could not be repeated with the former on account of the too great breadth of the longitudinal Doppler effect for interferometer work. With regard to his question as to the character of the many-lined spectrum in the positive rays, I can only say it is always fainter relative to the Balmer intensity than in the other parts of the discharge.

I am very grateful for Mr. Guild's remarks on the accuracy of the photometric wedge method, and for Mr. L. F. Richardson's suggestion of an important alternative method. The difficulties mentioned by Mr. Guild were increased by the curvature of the spectral line from a prism, and my only check on the accuracy was the comparison photographs without the wedge, taken to ensure at least an apparently even illumination of the whole length of the line.

DEMONSTRATION OF SOME SIMPLE EXPERIMENTS WITH THERMIONIC VALVES.

By E. H. Rayner, *Sc.D.*

A METAL plate or wire, connected to the grid of an ordinary receiving valve operating with 20 to 50 volts on the anode, acts as a sensitive indicator of the presence of an electric field in the neighbourhood. A piece of ebonite or sealing wax electrified by friction will cause an appreciable change in the anode current, when brought within 3 ft. or more of the conductor connected to the grid. A unipivot micro-ammeter or a reflecting galvanometer suitably shunted forms a satisfactory indicator. If such a negatively electrified object as ebonite is brought close to the grid conductor, the anode current may be reduced practically to zero, a positive charge being attracted to the near parts of the conductor and a negative charge being repelled to the grid. If the rod is quickly removed the anode current may flow momentarily, but cease again for several seconds, then gradually rise to the normal value. This does not happen with all valves, and it may be affected by the degree of insulation of the valve cap. If the electrified rod is removed somewhat more slowly the same valve may not show this second reduction of the anode current to zero, either effect being produced at will.

If a square piece of sealing wax is electrified and placed on a metal plate about 3 in. square connected to the grid, the anode current will be reduced to zero, with a suitable valve and anode voltage. It will gradually rise again to its normal value, which can again be reduced by turning the sealing wax so that another of the four sides touches the plate. Not only can this be done once with each of the four sides, but possibly several times over, the reason apparently being that the wax only touches the plate in a few points and these parts of it only are discharged by contact, and they become again charged by surface leakage from surrounding parts while the other three sides are being experimented upon. This effect was found to work well with a dull emitter valve which would not show the double reduction to zero of the anode current mentioned above.

In order to illustrate possible applications of induced grid electrification, a pendulum with a metal plate about 3 in. square was made to swing over a fixed similar plate with about a tenth of an inch clearance. The swinging plate was electrified by a battery of about 25 to 70 volts, one end of which was connected to the filament of the valve. A reversing switch was placed in the battery circuit, so that the pendulum could be either positively or negatively electrified. As the pendulum swings past the fixed plate, it affects the potential of the grid and increases or decreases the anode current twice every complete swing, according to the direction of the electrification. By suitably adjusting the conditions a variation of at least 2 : 1 in the current can be obtained. It sometimes happens that the first swing cuts the current down to zero for several seconds. It is not necessary to use such a large condenser as plates of the size mentioned. A horizontal piece of wire 4 in.

long projecting from the pendulum at right angles to the plane of its swing and passing over a similar fixed wire connected to the grid, with a clearance of a tenth of an inch or less, can be made to show quite an appreciable effect when electrified to 100-200 volts.

In general the use of a valve as an indicator of small relative displacements of metal surfaces which can be insulated from one another and charged to different potentials, seems to be one of some promise. When used with movements of the order of 1 or less periods a second, leakage in the valve cap becomes an important factor, and experiments of the type indicated are distinctly critical in showing up differences between valves.

OCT 4 1926

THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

VOLUME 38.—PART 5.
AUGUST 15, 1926.

Price to Non-Fellows **6s.** *net, post free* **6/3.**

Annual Subscription, **30/-** *post free, payable in advance.*

Published Bi-Monthly from December to August.

LONDON:

FLEETWAY PRESS, LTD.,
3-9, Dane Street, High Holborn, W.C.1.

1926.

THE PHYSICAL SOCIETY OF LONDON

1926-27.

OFFICERS AND COUNCIL.

President

PROF. O. W. RICHARDSON, M.A., D.Sc., F.R.S.

Vice-Presidents

(Who have Filled the Office of President.)

PRINCIPAL SIR OLIVER J. LODGE, D.Sc., F.R.S.
SIR RICHARD GLAZEBROOK, K.C.B., D.Sc., F.R.S.
C. CHREE, Sc.D., LL.D., F.R.S.
PROF. H. L. CALLENDAR, C.B.E., M.A., LL.D., F.R.S.
SIR A. SCHUSTER, Ph.D., Sc.D., F.R.S.
SIR J. J. THOMSON, O.M., D.Sc., F.R.S.
PROF. C. V. BOYS, F.R.S.
PROF. C. H. LEES, D.Sc., F.R.S.
PROF. SIR W. H. BRAGG, K.B.E, M.A., F.R.S.
ALEXANDER RUSSELL, M.A., D.Sc., F.R.S.
F. E. SMITH, C.B.E., D.Sc., F.R.S.

Vice-Presidents

PROF. F. LLOYD HOPWOOD, D.Sc.
D. OWEN, B.A., D.Sc.
E. H. RAYNER, M.A., Sc.D.
J. H. VINCENT, D.Sc., M.A.

Secretaries

PROF. A. O. RANKINE, O.B.E., D.Sc.
Imperial College of Science and Technology, S. Kensington, S.W.7.

J. GUILD, A.R.C.S., D.I.C., F.Inst.P.
Lalbagh, Park Road, Teddington, Middlesex.

Foreign Secretary

SIR A. SCHUSTER, K.B.E., Ph.D., Sc.D., F.R.S.

Treasurer

R. S. WHIPPLE
45, *Grosvenor Place*, S.W.1.

Librarian

J. H. BRINKWORTH, M.Sc., A.R.C.S.
Imperial College of Science and Technology, S. Kensington, S.W.7.

Other Members of Council

D. W. DYE, B.Sc.
A. FERGUSON, M.A., D.Sc.
E. A. OWEN, M.A., D.Sc.
SIR RICHARD PAGET, BART.
R. W. PAUL.
J. ROBINSON, M.Sc., Ph.D.
J. S. G. THOMAS, D.Sc.
W. S. TUCKER, D.Sc.
PROF. A. M. TYNDALL, D.Sc.
A. B. WOOD, D.Sc.

Assistant Secretary (Publications)

CAPT. C. W. HUME, M.C., B.Sc.
14, *The Hawthorns, Finchley*, N.3.

XXXIII.—STATIC AND ISOTROPIC GRAVITATIONAL FIELDS.

By G. TEMPLE, *Ph.D.*, Imperial College of Science.

Received March 8, 1923.

¶1. ABSTRACT.

The object of this Paper is to give a brief account of the principles of Einstein's General Theory of Relativity as applied to those problems in which they have received their most striking confirmation. To this end we have limited our investigations to the consideration of dynamical manifolds which are static and isotropic in character. It has then proved possible to abandon the notation and theory of the Absolute Differential Calculus, and to substitute in its place some classical theorems of Lord Kelvin and M. J. Liouville. Although the scope of these inquiries is not extensive, within the limits of our investigations we have explained the method of the construction and solution of Einstein's field equations, and have given the applications of these results to the problems of planetary motion and of the deviation of light rays in the solar gravitational field. At the same time we have endeavoured to make explicit the various assumptions involved in this theory.

I. THE LAWS OF MOTION.

¶2. *Particle Geodesics.*

THE first assumption which we make refers to the form in which we shall enunciate the law of motion of a mass-particle. The motion of a particle will be completely specified by the path which it describes together with the speed with which the path is traversed; and the complex of the spatial and temporal relations which are involved in this specification will be called the "route" of the particle. To determine the actual route pursued by a particle which is known to pass through the points A_1 and A_2 at times t_1 and t_2, we consider the qualifications of all possible routes which possess these fixed termini. With each possible route we associate an integral J, called, in Whitehead's terminology, the "realised impetus" of the route. Then we determine that route which possesses the two termini fixed above and which renders the impetus stationary, in the sense of the calculus of variations.

It is not an unreasonable assumption that the integral J may be defined in such a way that the route determined by this procedure is the actual route pursued by a particle which moves under the influence of a gravitational field, and which is subjected to the conditions of passing through the points A_1 and A_2 at times t_1 and t_2. Here we assume thot the element of impetus dJ associated with the element of route which is traversed by a particle of "proper" mass μ moving through an element of distance ds in time dt may be written in the form

$$dJ=\mu\,.\,dI=\mu(\omega^2\,.\,dt^2-\varphi^2\,.\,ds^2)^{\frac{1}{2}}, \qquad \ldots\ldots \quad (2{\cdot}1)$$

where dI may be called the "potential impetus," to distinguish it from the "realised impetus" dJ, and where ω and φ denote two real functions of the position of the particle at the instant considered, and express the properties of the gravitational field.

¶3. *Lagrangian Equations of Motion.*

In Cartesian co-ordinates x, y, z, the square of the element of distance may be written as

$$\begin{aligned} ds^2 &= dx^2+dy^2+dz^2 \\ &= (\dot{x}^2+\dot{y}^2+\dot{z}^2)\,.\,dt^2, \end{aligned}$$

where $\dot{x}, \dot{y}, \dot{z}$ denote the components of the velocity of the particle traversing the element of distance ds in time dt. The Lagrangian function for the particle may now be defined by the equation

$$L=\mu\{\omega^2-\varphi^2(\dot{x}^2+\dot{y}^2+\dot{z}^2)\}^{\frac{1}{2}}\ , \quad \dots\dots \quad (3\cdot1)$$

and the realised impetus along the route with termini at points A_1 and A_2 at times t_1 and t_2 may be written as

$$J=\int_{t_1}^{t_2} L\,.\,dt, \quad \dots\dots \quad (3\cdot2)$$

in virtue of equation (2·1). In this integral it is convenient to suppose that the various possible routes which possess the termini fixed above are prescribed by taking x, y, z to be arbitrary functions of t, which reduce, when $t=t_1$ or t_2 to the co-ordinates of the points A_1 or A_2. The conditions that the integral should be stationary are expressed by the three Lagrangian equations

$$\frac{d}{dt}\cdot\left(\frac{\partial L}{\partial\dot{\theta}}\right)=\frac{\partial L}{\partial\theta} \quad \dots\dots \quad (3\cdot3)$$

where θ stands for any one of the co-ordinates x, y, z.

¶4. *Permanent Gravitational Fields.*

The functions ω and φ will be explicitly independent of the time t if the gravitational field is permanent, and we may then deduce two important corollaries to the equations (3·3) of the preceding paragraph.

In the first place, we may infer at once that the initial acceleration **a** of a particle starting from rest is given by the vector equation

$$\mathbf{a}=-\tfrac{1}{2}\varphi^{-2}\,.\,\mathrm{grad.}(\omega^2) \quad \dots\dots \quad (4\cdot1)$$

In the second place, the path described by the particle may be found by introducing an auxiliary variable τ defined by the equation

$$c\,.\,\tau=\int\varphi^{-2}\,.\,dI \quad , \dots\dots \quad (4\cdot2)$$

in which the integral is taken along the route described by the particle from some convenient terminus, and in which the constant c is inserted to ensure that the variables τ and t have the same dimensions and approximately the same magnitude (*see* ¶6). On using dashes to denote differentiation with respect to τ, we may replace the Lagrangian function L of the last paragraph (3·1) by the modified Lagrangian function Λ defined by the equation

$$\Lambda=\mu\{\omega^2 . t'^2-\varphi^2(x'^2+y'^2+z'^2)\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·3)$$

on the understanding that x, y, z, t, are now prescribed as functions of τ. The integral of impetus may be written in the form

$$J=\int_{\tau_1}^{\tau_2} \Lambda . d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·4)$$

where τ_1 and τ_2 are the values of τ at the termini of the route. The four modified Lagrangian equations will be

$$\frac{d}{d\tau}\left(\frac{\partial\Lambda}{\partial\theta'}\right)=\frac{\partial\Lambda}{\partial\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·5)$$

where θ stands for any one of the co-ordinates x, y, z, t.

From equations (2·1), (4·4) and (4·2) we deduce that

$$\mu . dI\equiv dJ\equiv\Lambda . d\tau\equiv\Lambda c^{-1}\varphi^{-2} . dI,$$

whence

$$\Lambda=\mu c\varphi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·6)$$

But ω and φ are explicitly independent of t and τ, so that the fourth modified Lagrangian equation obtained by writing $\theta=t$ in (4·5) yields the results

$$\frac{\partial\Lambda}{\partial t}=0 \text{ and } \frac{\mu^2\omega^2t'}{\Lambda}=\frac{\partial\Lambda}{\partial t'}=\text{a constant},$$

whence $\omega^2t'=c^2p\varphi^2$ from equation (4·6), where p is a constant related to the velocity of projection, u_1, in the manner indicated by the equation (derived from (4·3) and (4·6))

$$p=\frac{\omega_1}{c}\left\{1-\frac{\varphi_1^2}{\omega_1^2}u_1^2\right\}^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·7)$$

in which the suffixes show that the arguments of the functions φ and ω are the co-ordinates of the point of projection.

The three modified Lagrangian equations obtained by setting $\theta=x, y, x$ in (4·5) now yield the results

$$x'', y'', z''=-\frac{\partial U}{\partial x,\ y,\ z,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·8)$$

where

$$U=\tfrac{1}{2}\varphi^2c^2\left\{\frac{1-c^2p^2}{\omega^2}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4·9)$$

Hence, when we know the circumstances of the projection of a particle, we may evaluate the constant p by means of the equation (4·7), and then construct the corresponding function U by means of equation (4·9). The three equations (4·8) then show that the actual path which is described by the particle is identical with that which would be traversed if the particle were moving in a Newtonian field of force of potential U.

II. THE FIELD EQUATIONS.

¶5. *Invariant Equations for Permanent Gravitational Fields.*

The second assumption which we make refers to the form in which we shall enunciate the equations of the gravitational field which determine the functions ω and φ. We shall assume that these equations contain no derivatives of ω or φ of orders higher than the second, and that the equations are linear in the second derivatives. The determination of the equations is then completed by the further hypothesis that they shall retain the same form in any set of co-ordinates which preserves the form of dI^2 given in equation (2·1), viz. :—

$$\omega^2 . dt^2 - \varphi^2(dx^2+dy^2+dz^2)$$

As we are considering statical fields only, we need study the effect of changes in the spatial co-ordinates alone. It will be recognised at once that such transformations in x, y, z as translations and rotations preserve the form of dI^2, and leave invariant the functions ω and φ together with the expressions $\delta\omega$ and $\delta\varphi$, in which δ denotes the Laplacian operator

$$\delta \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Other quantities which are unaffected in form or magnitude by these transformations are the three scalar products (grad. ω, grad. ω), (grad. ω, grad. φ), (grad. φ, grad. φ) ; and a great variety of invariant equations satisfying the criteria laid down above may be constructed out of these invariants, the functions ω and φ, and the quantities $\delta\omega$ and $\delta\varphi$.

The quadratic expression $\varphi^2(dx^2+dy^2+dz^2)$ (which is now written more conveniently as $\psi^4(dx^2+dy^2+dz^2)$, so that $\varphi=\psi^2$) also remains unaltered in form when the variables x, y, z are subjected to magnifications or inversions, and, although all the invariants of the last paragraph, except ω, now lose that character, we may construct combinations of them which still retain invariant form and magnitude for these fresh types of transformations. Considering only inversions whose pole is at the origin of the co-ordinate system, we denote the new variables by X, Y, Z, and the radius of inversion by a, so that

$$X : x = Y : y = Z : z = a^2 : r^2 = R^2 : a^2, \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

where $\quad r^2=x^2+y^2+z^2,$

and $\quad R^2=X^2+Y^2+Z^2.$

If $\triangle$ denotes the Laplacian operator in the new co-ordinates, so that

$$\triangle \equiv \frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}$$

it is easily established by direct transformation that if

$$f(x, y, z)=F(X, Y, Z),$$

then $\quad \triangle F=\frac{r^5}{a^5}\delta\left(\frac{af}{r}\right).$

An immediate corollary to this theorem of Lord Kelvin s is obtained by noting that if

$$\psi^4(dx^2+dy^2+dz^2)=\Psi^4(dX^2+dY^2+dZ^2),$$

then

$$\psi=\frac{a}{r}.\,\Psi,$$

whence

$$\frac{\delta\psi}{\psi^5}=\frac{\Delta\Psi}{\Psi^5}. \qquad \text{(5·2)}$$

We have thus obtained one quantity $(\psi^{-5}.\,\delta\psi)$ which remains invariant for inversions. A second may be constructed on remarking that the relations (5·1) imply also that

$$r\,.\,R=a^2$$

$$r\,.\,\psi^2=R\,.\,\Psi^2$$

while

$$\frac{1}{r^2\psi^6}\cdot\frac{\partial}{\partial^2}=\frac{-1}{R^2\Psi^6}\cdot\frac{\partial}{\partial R}.$$

By transformations in spherical polars it may now be shown that

$$\psi^{-6}\,\text{div.}\,(\psi^2\,\text{grad.}\,\omega)=\Psi^{-6}\,.\,\text{DIV.}\,(\Psi^2\,.\,\text{GRAD.}\,\omega), \qquad \text{(5·3)}$$

where the capitals DIV. and GRAD. denote the vector operators in the co-ordinates X, Y, Z, analogous to the vector operators div. and grad. in the co-ordinates x, y, z.

It is now easily seen that the functions $\psi^5\,.\,\delta\psi$ and $(\omega\psi^6)^{-1}\,.\,\text{div.}\,(\psi^2\,\text{grad.}\,\omega)$, are also invariant for magnifications, as well as for all the other types of transformation studied above. From the well-known researches of Lord Kelvin and M. J. Liouville,* it is known that those transformations exhaust the possible types which leave invariant the equation

$$dx^2+dy^2+dz^2=0,$$

and the form of the expression

$$\psi^4(dx^2+dy^2+dz^2).$$

And it may also be shown that every invariant, which satisfies the criteria laid down above, must be a linear function of the two invariants which we have found. Hence the most general invariant equations for permanent isotropic gravitational fields are

$$\left.\begin{aligned}\delta\psi&=\lambda_1\,.\,\psi^5,\\ \text{and}\qquad \text{div.}\,(\psi^2\,\text{grad.}\,\omega)&=\lambda_2\omega\psi^6\end{aligned}\right\} \qquad \text{(5·4)}$$

where λ_1 and λ_2 are constants.

A reference to a classical memoir of Levi-Cività† will show that in his notation we may write

$$M=-4\psi^{5}\,.\,\delta\psi$$

and

$$\Delta_2\omega=\psi^{-6}\,.\,\text{div.}\,(\psi^2\,\text{grad.}\,\omega),$$

so that our equations are

$$\left.\begin{aligned}M&=-4\lambda_1\\ \text{and}\qquad \Delta_2\omega&=\lambda_2\omega\end{aligned}\right\} \qquad \text{(5·5)}$$

---

* " Extraits de deux Lettres adressées à M. Liouville par M. William Thomson." " Note au sujet de l'article précédent, par J. Liouville," pp. 256-264 and 265-290, Journal de Mathématiques pures et appliquées, Tome XII. (1847).

† T. Levi-Cività, " Statica Einsteiniana," Atti d. Reale Accad. d. Lincei, Roma, Serie (5), 1917. Tom. 26 (1), pp. 458-470.

¶6. *Supplementary Conditions.*

The two equations (5·4) or (5·5) of the last paragraph will take the place in this Paper of the seven equations given by Levi-Civitá (provided we take λ_1 and λ_2 to be zero, as in Einstein's earlier theory). The determinations of the functions ω and φ will be completed by assigning suitable boundary conditions and two additional assumptions.

The first of these assumptions (and the third employed in this Paper) is an extension of the hypothesis of ¶2. There we assumed that the routes traversed by material particles were the geodesics of the quadratic differential form

$$dJ^2=\mu\{\omega^2dt-\varphi^2(dx^2+dy^2+dz^2)\}.$$

Among these geodesics we may single out for special mention those which also satisfy the condition

$$dJ=0.$$

These "null-routes," along which the impetus is zero, we assume to be the tracks of rays of light.

Since along these routes dI and $d\tau$ (by (4·2)) are zero, we must write their equations in the forms of ¶3 rather than in the modified forms of ¶4. Thus, we deduce at once from equations (3·1) and (3·2) that along a "null-route"

$$L=0,$$

while the velocity of propagation of the ray of light is

$$(\dot{x}^2+\dot{y}^2+\dot{z}^2)=\frac{\omega}{\varphi} \qquad \text{(6·1)}$$

Since this velocity is independent of the direction of propagation the field is said to be "isotropic."

The last assumption that we make is that as we recede from regions of space occupied by matter, the effects of gravitational influence diminish, in such a way that at considerable distances the gravitational field is sensibly Newtonian in character, while the velocity of light is sensibly equal to 3×10^{10} cms./sec., a constant denoted by c.

It is evident that the multiplication of ω and φ by the same number will have no influence on the form of the routes of mass-particles or rays of light. As a convention, therefore, we shall make $\varphi\rightarrow1$ as $x, y, z\rightarrow\infty$. Then, from equation (6·1) and our last assumption we see that under these conditions $\omega\rightarrow c$ and $dI\rightarrow c.dt$. We thus justify the inclusion of the constant c in equation (4·2).

Even now the determination of the functions ω and ψ is not unique; for it will be seen that if V is any Newtonian potential satisfying the equation

$$\delta\,.\,V=0,$$

then, since $r.V$ and r^2 grad. V both tend to constant values as we recede from the regions occupied by matter, approximate solutions of the gravitational equations (5·4) when λ_1 and λ_2 are zero, are

$$\left.\begin{aligned}\psi&=1+\kappa_1V\\ \text{and}\qquad \omega&=c(1+\kappa_2V)\end{aligned}\right\} \qquad \text{(6·2)}$$

To identify the constant κ_2 we observe that the initial acceleration of a particle as given by equation (4·1) is

$$\mathbf{a} \sim -c \text{ grad. } \omega = -c^2\kappa_2 \text{ grad. } V,$$

whence κ_2 must be c^{-2} in order that we may satisfy the last assumption of this paragraph. But we still have no means by which we may determine the constant κ_1. To identify this constant we have recourse to the cosmological theory of the succeeding paragraph.

¶7. *Cosmological Theory.*

We have hitherto supposed that the element of distance between two points is given by the Euclidean relation

$$ds^2 = dx^2 + dy^2 + dz^2 ;$$

but if we suppose that a better representation of the phenomena may be obtained with non-Euclidean geometry, we must replace this equation by

$$ds^2 = \frac{dx^2 + dy^2 + dz^2}{(1 + r^2/4R^2)^2}, \qquad \text{. . . . . (7·1)}$$

where R is the "space-constant" (determining the "size" of the universe) and $r^2 = x^2 + y^2 + z^2$.

Now the function $\psi = (1 + r^2/4R^2)^{-\frac{1}{2}}$ is a solution of the equation

$$M = 3 . R^{-2},$$

and we shall accordingly adopt this relation as one of the field equations in non-Euclidean space.

To obtain the appropriate value of the constant λ_2 in the second equation (5·5) we note that if θ and ϕ are the usual angular co-ordinates in the spherical polar system, while

$$r = 2R . \tan \tfrac{1}{2}\chi,$$

then

$$ds^2 = R^2 d\chi^2 + R^2 \sin^2\chi (d\theta^2 + \sin^2\theta . d\phi^2). \qquad \text{. . . (7·3)}$$

Hitherto, our expression for dI^2, the square of the linear element of the dynamic manifold, has had the limiting form (see ¶6), as $x, y, z \to \infty$.

$$dI^2 = c^2 dt^2 - (dx^2 + dy^2 + dz^2),$$

but now, following de Sitter,* we shall take as the limiting form

$$\begin{aligned} dI^2 &= \cos^2\chi . c^2 dr^2 - R^2 d\chi^2 - R^2 \sin^2\chi (d\theta^2 + \sin^2\theta . d\phi^2) \\ &= \omega^2 . dr^2 - \psi^4 (dx^2 + dy^2 + dz^2), \end{aligned}$$

where

$$\left.\begin{aligned} \psi &= (1 + r^2/4R^2)^{-\frac{1}{2}}, \\ \text{and} \quad \omega &= c \cos \chi = c \frac{1 - \dfrac{r^2}{4R^2}}{1 + \dfrac{r^2}{4R^2}} \end{aligned}\right\} \qquad \text{. . . . . . (7·4)}$$

---

* A. S. Eddington, "The Mathematical Theory of Relativity," 1923. § 67, "Cylindrical and Spherical Space-time."

This function satisfies the equation

$$\frac{\Delta_2\omega}{\omega} = -3R^{-2}, \qquad \ldots\ldots\ldots\ldots \qquad (7{\cdot}5)$$

which we shall therefore take to be the second field equation in non-Euclidean space.

From the values of ψ and ω, given in equation (7·4), and by the use of equation (4·1), we find that the initial acceleration of a particle is

$$\frac{c}{R^2}r\omega$$

indicating the tendency to scatter shown by the high recessive velocities of spiral nebulæ.

To complete the determination of the constants λ_1 and λ_2 of the preceding paragraph, we construct the complete integrals of equations (7·2) and (7·5), on the assumption that ψ and ω are functions of r only. The solutions thus obtained apply to the regions of space remote from matter. The first equation (7·2) may be written as

$$\frac{1}{\psi^5}\left(\frac{d^2\psi}{dr^2}+\frac{2}{r}\frac{d\psi}{dr}\right)+\frac{3}{4R^2}=0$$

and possesses an integrating factor

$$4r^2\psi^5\left(\psi+2r\frac{d\psi}{dr}\right)$$

by means of which we obtain the first integral

$$4r^3\left(\frac{d\psi}{dr}\right)^2+4r^2\psi\frac{d\psi}{dr}+\frac{\psi^6r^3}{R^2}=-2m,$$

where m is a constant integration. This equation may also be written in the form

$$\frac{d}{dr}(r\psi^2)=\psi^2.\left(1-\frac{2m}{\psi^2r}-\frac{\psi^4r^2}{R^2}\right)^{\frac{1}{2}}$$

To complete the solution, we introduce a new variable ρ, defined by the relation

$$\rho=r\psi^2 \qquad \ldots\ldots\ldots\ldots \qquad (7{\cdot}61)$$

and the function

$$\gamma=1-\frac{2m}{\rho}-\frac{\rho^2}{R^2} \qquad \ldots\ldots\ldots\ldots \qquad (7{\cdot}62)$$

whence

$$\frac{d\rho}{dr}=\frac{\rho}{r}\sqrt{\gamma} \qquad \ldots\ldots\ldots\ldots \qquad (7{\cdot}63)$$

and

$$\psi^4(dr^2+r^2d\theta^2+r^2\sin^2\theta\,.\,d^2\phi)=\frac{d\rho^2}{\gamma}+\rho^2d\theta^2+\rho^2\sin^2\theta d\phi^2 \qquad \ldots \qquad (7{\cdot}64)$$

If an explicit expression for ρ is required, we deduce from equation (7·63) that

$$\log\frac{r}{r_0}=\int^{\rho_0}\frac{d\rho}{\rho\sqrt{\gamma}} \qquad \ldots\ldots\ldots\ldots \qquad (7{\cdot}65)$$

(where ρ_0 is the larger positive root of the equation $\gamma=0$). So that ρ may be expressed in terms of r by means elliptic functions.

The second equation (7·5) may be written as

$$\frac{d}{dr}\left(r^2\psi^2\frac{d\omega}{dr}\right)=-\frac{3r^2\psi^6\omega}{R^2};$$

or, on changing the independent variable from r to ρ, as

$$\frac{d}{d\rho}\left(\gamma^{3/2}\frac{d}{d\rho}(\gamma^{-\frac{1}{2}}.\,\omega)\right)=0$$

whence the complete integral is seen to be

$$\omega=A\,.\,\sqrt{\gamma}+B\sqrt{\gamma}\int_0\gamma^{-3/2}.\,d\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7\cdot7)$$

We have now four arbitrary constants of integration to identify—the A and B of (7·7), the m which occurs in γ (7·62) (and hence in ρ, ψ and ω), and the r_0 of (7·65). Now in the absence of a gravitational field, as we see from the particular solutions of (7·4), $m=0$, while

$$\rho=r\,.\,(1+r^2/4R^2)^{-1}$$

and

$$\gamma=1-\rho^2/R^2$$

Even when a gravitational field is present, the effects of such a field in regions remote from the attracting matter, say where $\rho\sim R$ or $r\sim 2R$, must be negligible compared with the effects of space curvature. Hence to determine r_0 in (7·65) we assume that ψ is approximately equal to $(1+r^2/4R^2)^{-\frac{1}{2}}$, when r is approximately $2R$. Then r_0 must be 2R. To determine A and B in (7·7) we assume that ω is approximately equal to $c\dfrac{1-r^2/4R^2}{1+r^2/4R^2}$ when $r\sim 2R$. Then B must be zero (for the integral is divergent), while $A=c$. Hence the admissible integrals are

$$\psi=\sqrt{\rho/r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7\cdot81)$$

where ρ is defined by the integral

$$\log\frac{r}{2R}=\int^{\rho_0}\frac{d\rho}{\rho\sqrt{\gamma}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7\cdot82)$$

and

$$\omega=c\sqrt{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7\cdot83)$$

In regions where gravitational effects are of the first order of infinitesimals, while curvature effects are of the second order of infinitesimals—i.e., $\dfrac{2m}{\rho}$ is small compared with unity, while $\dfrac{\rho^2}{R^2}$ is small compared with $\dfrac{2m}{\rho}$, we have the approximations

$$\left.\begin{aligned} r&\sim\rho-m\\ \psi&\sim 1+\frac{m}{2r}\\ \text{and}\qquad \omega&\sim c\left(1-\frac{m}{r}\right)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7\cdot9)$$

If the total mass of attracting matter is M, the Newtonian potential will be approximately

$$V \sim -\frac{\gamma M}{\varepsilon} \text{ (where } \gamma \text{ is now the constant of gravitation)}$$

Hence by comparing equations (7·9) and (6·2) we see that.

$$m = -\gamma \frac{M}{c^2}$$

$$\kappa_1 = -\frac{1}{2c^2} \text{ and } \kappa_2 = \frac{1}{c^2}$$

III. THE SOLAR FIELD.

¶8. *Solution of the Field Equations.*

In applying the general methods of the preceding paragraphs to the particular problems of the solar gravitational field, we take the centre of the sun as the origin of a system of polar co-ordinates of radius vector r; and we assume that the gravitational field of the sun has spherical symmetry, so that the functions ω and φ depend only upon r. The general equations of the field (5·4) now simplify to

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=0$$

and

$$\frac{d}{dr}\left(r^2\psi^2\frac{d\omega}{dr}\right)=0$$

The general solutions of these equations, subject to the boundary conditions

$$\psi \to 1 \text{ and } \omega \to c \text{ as } r \to \infty$$

are

$$\psi=\left(1+\frac{m_1}{2r}\right)$$

and

$$\omega = c\frac{1-\frac{m_2}{2r}}{1+\frac{m_1}{2r}} \sim c\left(1-\frac{m_1+m_2}{2r}\right),$$

where m_1 and m_2 are constants of integration.

The application of the general results of the last paragraph (equation (7·9)) now shows that if M is the mass of the sun and γ is the constant of gravitation,

$$m_1 = m_2 = m = \frac{\gamma M}{c^2}$$

We have thus obtained Hill and Jeffery's solution of Einstein's equations*

$$\left.\begin{aligned}\psi &= \left(1+\frac{m}{2r}\right)\\ \text{and} \quad \omega &= c\frac{1-\frac{m}{2r}}{1+\frac{m}{2r}}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (8·1)$$

---

* F. W. Hill and G. B. Jefery, "The Gravitational Field of a Particle on Einstein's Theory," Phil. Mag. (6), Vol. 41, pp. 823-826 (1921).

whence

$$dl^2=\left(\frac{1-\frac{m}{2r}}{1+\frac{m}{2r}}\right)^2 c^2dt^2-\left(1+\frac{m}{2r}\right)^4(dr^2+r^2d\theta^2+r^2d\phi^2)$$

(in spherical polar co-ordinates r, θ, ϕ).

We may also deduce these results from the general " cosmological " solutions of (7·81, 7·82 and 7·83) by making $R \rightarrow \infty$.

¶9. *Planetary Orbits.*

To determine the forms of the orbits described by planets in the solar field, we assume that to a first approximation we may neglect their mutual perturbations, and that we may regard them as particles. We then apply the general results established in ¶4. Since planetary velocities are small compared with the velocity of light, the constant p of equation (4·7) may be taken to be unity, and the " apparent Newtonian potential " U of equation (4·9) may then be written in terms of $u=1/r$, as

$$U\sim\frac{c^2}{2}\left(1+\frac{1}{2}\,mu\right)^4-\frac{c^2}{2}\left(1+\frac{1}{2}\,mu\right)^6\cdot\left(1-\frac{1}{2}mu\right)^{-2}$$

(in virtue of equations (8·1))

$$=-c^2(mu+3m^2u^2)\qquad\ldots\ldots\ldots\ldots\qquad(9\cdot1)$$

neglecting powers of $(m\,.\,u)$ above the second, an approximation justified, since for the sun $m=1{\cdot}47$ km., and for mercury $u^{-1}=5{\cdot}77\times10^7$ km.

The path described by a planet is found now just as in classical dynamics, provided that the variable τ of equation (4·2) is treated as the " time " and that U is treated as the " potential." Since U is a function of r only, the path will be plane and will be traversed with uniform areal " velocity "

$$\frac{1}{2}r^2\frac{d\theta}{d\tau}=\frac{1}{2}h$$

(using θ to denote the angle which the radius vector of the planet makes with any fixed line in the plane of the orbit). The apparent central acceleration will be

$$P=\frac{dU}{dr}=-u^2\frac{dU}{du}$$

and the equation to the orbit is therefore

$$\frac{d^2u}{d\theta^2}+u=\frac{-P}{h^2u^2}$$

$$=\frac{mc^2}{h^2}(1+6mu)\text{ from equation }(9\cdot1)\qquad\ldots\ldots\ldots\qquad(9\cdot2)$$

The solution of this equation (an especial case of " Newton's revolving orbits " is)

$$l\,.\,u=1+\varepsilon\cos\kappa\theta$$

where

$$\frac{lmc^2}{h^2}=\kappa^2=1-\frac{6m^2c^2}{h^2}.$$

and represents an ellipse, focus at the sun, semi-latus-rectum l and eccentricity ε, revolving in its own plane, so that the perihelion advances

$$\frac{2\pi}{\kappa}-2\pi\sim\frac{6\pi\gamma M}{c^2 l} \text{ radians per complete revolution of the planet.}$$

¶10. *Light Rays.*

Apart from a constant factor, the Lagrangian function of (3·1) may be written in polar co-ordinates as

$$L=\{\psi^2-\varphi^2(\dot{r}^2+r^2\dot{\theta}^2)\}^{1/2}$$

It has been explained in ¶6 that the paths of rays of light are determined from those special solutions of the Lagrangian equations

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \varepsilon}\right)=\frac{\partial L}{\partial r} \text{ and } \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right)=\frac{\partial L}{\partial \theta} \quad \ldots\ldots\ldots \quad \text{(cf. eq. 3·3)}$$

which also satisfy the relation (6·1)

$$v^2=\dot{r}^2+r^2\theta^2=\omega^2\varphi^{-2} \quad \ldots\ldots\ldots\ldots \quad (10·1)$$

In the solar gravitational field, it is evident that we may limit ourselves to the consideration of paths which lie in a plane passing through the centre of the sun, and such that ω and φ will depend only upon the radius vector r. Hence the second of the Lagrangian equations given above yields the integral

$$\varphi^2 . r^2\dot{\theta} . L^{-1}=\text{const.} \quad \ldots\ldots\ldots \quad (10·2)$$

Also from equation (4·7) we obtain the relation

$$\omega^2 . L^{-1}=\text{const.} \quad \ldots\ldots\ldots\ldots \quad (10·3)$$

Although both of these equations become illusory when $L=0$, we may still obtain an effective relation by equating the ratios of corresponding sides, when we obtain

$$\varphi^2 . \omega^{-2} . \dot{\theta}r^2=\text{const.} \quad \ldots\ldots\ldots \quad (10·4)$$

That this constant is finite may be deduced from equation (10·1) by noticing that when $\dot{r}=0$—i.e., at an apse (say, when $r=r_0$), then

$$r\dot{\theta}=\omega_0 . \varphi_0^{-1}$$

whence the constant of (10·4) is seen to be $r_0\varphi_0\omega_0^{-1}$ (the suffixes showing that the arguments of the functions ω and φ are both r_0).

The equation to the path of a ray of light is now obtained by substituting in (10·1)

$$r=1/u,\ \dot{r}=-r^2\theta^2 . du/d\theta$$

and the value of $\dot{\theta}$ given by equation (10·4). We thus obtain

$$\left(\frac{du}{d\theta}\right)^2+u^2=\frac{\varphi^2}{\varphi_0^2} . \frac{\omega_0^2}{\omega^2} . u_0^2$$

$$=u_0^2 . (1+4mu-4mu_0) \quad \ldots\ldots\ldots \quad (10·5)$$

to our degree of approximation. The solution of this equation is

$$u=2mu_0^2(1+\varepsilon\cos\theta)$$

where $$\varepsilon\sim 1/2mu_0^2$$

showing that the path is an hyperbola of eccentricity ε. Hence the angle between the asymptotes of the hyperbola, which gives the angular deviation of the light from a distant star, is $4mu_0$ radians.

¶11. *Conclusion.*

In this brief sketch of one of the theories of relativity, the three equations of motion of a particle given by Newton's theory are replaced by the three equations of (4·8); while the Laplacian equation satisfied by the Newtonian potential is replaced by the two equations (5·5), satisfied by the two functions ω and φ; so that as close an analogy as possible has been maintained with the principles and methods of classical dynamics. Unfortunately, in order to obtain suitable qualitative boundary conditions, it has been necessary to introduce de Sitter's cosmological theory and " spherical space time." With this single exception, the argument follows the lines of Einstein's General Theory and issues in the same conclusions.

DISCUSSION.

Prof. W. WILSON said that he cordially welcomed the reading of Papers of the present kind to the Physical Society, but he questioned whether the author's method was as simple in principle as that of Schwarzschild, in spite of its saving of laborious computation. The practice of regarding an event-path as a geodesic had been referred to by the author as an " assumption," but he would like to ask what significance could be attached to a path which was not a geodesic.

Dr. C. CHREE referred to some outstanding analytical problems which were insoluble, or soluble only with difficulty, by the classical mechanics, and inquired whether the forms of calculus brought into prominence by the theory of relativity had provided simpler methods of dealing with any of these.

AUTHOR'S REPLY (communicated).—In reply to Dr. Wilson: Schwarzschild's problem was the *solution* of the gravitational equations $G_{\mu\nu}=0$ in a static field possessing spherical symmetry; the object of this Paper is the *construction* of the gravitational equations in a static and isotropic field; hence the problems are of different characters. Deviations from geodesic paths may be attributed (if the moving particle is charged) to the influence of electromagnetic fields.

In reply to Dr. Chree, I quote from MM. Ricci and Levi-Civitâ (Math. Ann., Band 54, 1900, S.159): " Ces méthodes (de calcul différentiel absolu) n'ont pas la prétention d'éliminer les difficultés essentielles aux questions auxquelles elles sont appliquées. Au contraire, elles ne conduisent qu'à des transformations d'équations laissant nécessairement subsister toutes ces difficultés."

XXXIV.—ON THE DIFFRACTION OF LIGHT BY SPHERICAL OBSTACLES.

By Prof. C. V. RAMAN, *F.R.S.*, and Mr. K. S. KRISHNAN.

ABSTRACT.

The diffraction of light inside the shadow, thrown by a small source of light, of a sphere and a circular disc of the same diameter, was studied, with special reference to the relative intensities of the central bright spots. With the source at about 2 metres from the obstacles, with a quarter-inch polished steel ball, the bright spot could be detected visually up to 3 cm. behind the obstacle, while with a steel disc of the same diameter, with the edges perfectly sharp, smooth and circular, the spot could be traced up to 2 cm.

The relative intensities of the two spots were studied at different distances behind the obstacles, qualitatively by photography and quantitatively by visual photometry. At small distances behind the obstacles, the spot inside the shadow of the sphere is much feebler than the disc-spot, however approximating to the latter as we reach farther back from the obstacles, but even at 100 cm. remaining appreciably feebler.

A general explanation is suggested.

I. INTRODUCTION.

IT has long been known* that at the centre of the shadow of a spherical obstacle thrown by a small source of light there is a bright spot similar to that found in the shadow of a circular disc; and, in fact, a spherical obstacle is often used instead of a disc to demonstrate the formation of the bright spot at the centre of the shadow of a circular boundary. It is usually assumed by experimenters† that at a point on the axis of the shadow a circular disc and a sphere of equal radius would give practically identical results. This, however, is not actually the case, and it is the purpose of this Paper to draw attention to the notable differences that exist between the effects observed in the two cases.

II. THE INTENSITY OF THE BRIGHT SPOT.

To compare the effects obtained in the shadow of a spherical obstacle and a circular disc of equal size, it is convenient to mount them side by side on a glass plate, so that the bright spots at the centres of their shadow may be seen at the same time. In most of our observations we used a quarter-inch (diameter) steel ball and an accurately made steel disc of the same size, cut on the lathe so as to have a sharp circular edge of razor-like smoothness and sharpness. They were attached by specks of wax, with sufficient space between them, to a glass plate, and held at a distance of about two metres from the source.

The diffraction patterns within the shadow of disc and sphere were seen simultaneously through a lens of sufficiently wide field of view. When a bright source of light is used, it is convenient to use a plate with two holes cut in it, to correspond with the shadow of the sphere and the disc, and place it in the field of view so as to cut off all extraneous light except that diffracted into the region of shadow. The removal of the glare outside the region of shadow is very helpful, and with this

---

* Rayleigh, Sc. Papers, Vol. V, p. 112. *See* also A. O. Rankine, Proc. Phys. Soc., Vol. 37, p. 267 (1925).

† Hufford, Phys. Rev., Vol. 7, p. 545 (1916).

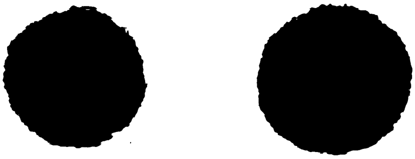


FIG. 1.

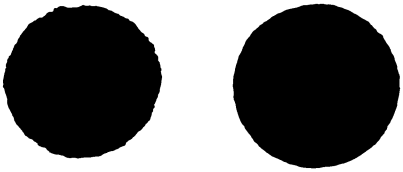


FIG. 2.

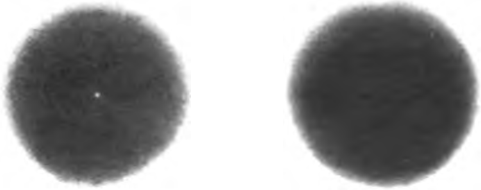


FIG. 3.

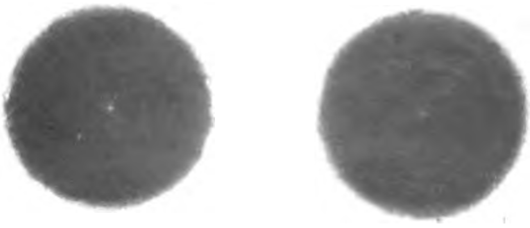


FIG. 4.

[*To face page* 351

arrangement it is possible to trace the bright spots in the centre of the shadow up to within 3 cm. of the object in the case of the sphere, and to less than 2 cm. in the case of the disc, thus testifying to the accuracy of the edges. A series of photographs were taken of the diffraction patterns with the source of light 179 cm. in front of the obstacles, and with the object plane of the camera at different distances behind them. Some of these are reproduced here (Figs. 1, 2, 3, 4). In the photographs the diffraction pattern on the right corresponds to the sphere and that on the left to the disc. We can easily see that the central white spots in the case of the sphere are much less bright than in the case of the disc. Thus, in Fig. 1, which corresponds to a distance of about 11 cm. behind the obstacles, the spot in the case of the sphere is invisible in the photograph. At 13 cm., as shown in Fig. 2, it is just visible. At 25 cm. (Fig. 3) it is still much feebler than for the disc, and at 40 cm. (Fig. 4) the difference in intensity of the two bright spots is still conspicuous. Further, we see in the photographs that the general illumination within the geometrical shadow is much greater for the disc than for the sphere. The spots in the shadow of the sphere were distinctly reddish in comparison with those for the disc, and the photographic intensity thus differed more than the visual intensity.

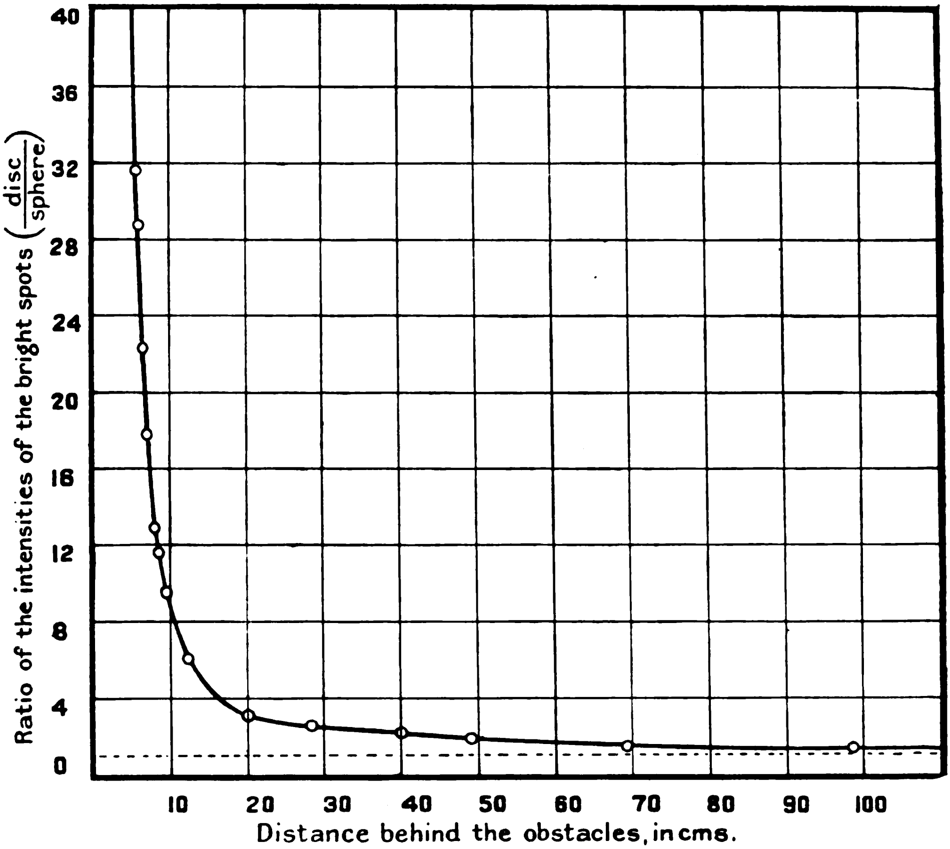


FIG. 5.

A quantitative study of the relative intensities of the central white spots of the two diffraction patterns was made with the help of an Abney rotating sector photometer placed just in front of the obstacles, and looking for the diffraction patterns through the eye-glass with the two apertures in its focal plane, mentioned already. The source of light was at a distance of 232 cm. in front of the obstacles. The results are shown in the graph on p. 351 (Fig. 5). Owing to the difference in colour, some uncertainty arises in the visual estimates of equality of intensity. Further, for short distances behind the obstacles the comparison was by no means easy, owing to the spots having a very small size, and appearing against a luminous background. Owing to these circumstances, the measurements shown in the graph are only approximate. Nevertheless, they sufficiently indicate the general character of the phenomenon. The dotted line in Fig. 5 is the asymptote to the curve, and is slightly above the line of equality of intensities.

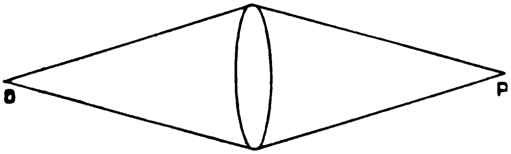


FIG. 6*a*.

III. DISCUSSION OF RESULTS.

Without going into the mathematical theory of diffraction by a spherical obstacle, it is not difficult to give a general physical explanation of the above experimental results. In the case of the disc (Fig. 6*a*) the rays diffracted by the illuminated edge reach the point of observation directly. In the case of the sphere, however, the position is somewhat different. Drawing tangent cones enveloping the spherical obstacle, with the source and the point of observation as apexes (Fig. 6*b*), we see that they now touch the sphere at different circles of contact, X and Y respectively. Thus, the circle of contact Y, from which diffracted rays originating at the surface can reach the point of observation, lies within the region of geometrical shadow, and not at its edge, as in the case of the disc. The disturbance incident on the surface of the sphere has to creep round it, as it were, over the arc XY before the rays diffracted out by the sphere can reach the point of observation, and must suffer a very considerable diminution in the process. Thus, we can see that the intensity of the central white spot in the diffraction pattern of a sphere will be less than in the case of the disc at the same distance behind by a quantity depending on the length of the arc XY between the circles of contact of the tangentially incident and diffracted rays. Now the length of this arc will be the greater the nearer the point of observation

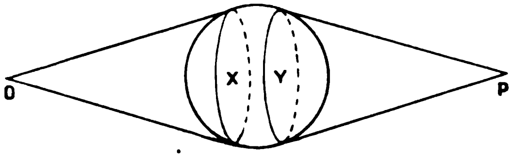


FIG. 6*b*.

approaches the sphere, so that the intensity of the sphere-spot, as compared with the disc-spot, ought to decrease as we approach the obstacles. Proceeding in the opposite direction, the intensity at large distances will approach that of the dfsc, but still will be smaller than the latter by an amount which will depend on the distance of the source from the obstacle.

That the foregoing way of viewing the matter is not fanciful, but is really a statement of the physical processes occurring in the case, is evident from the following observations. A microscope is focussed tangentially on the circle of contact X already mentioned, which appears as a luminous edge in the field of view. If now the microscope is shifted laterally into the region of the geometrical shadow, we find that it has also to be drawn back longitudinally towards Y in order to keep the diffracting edge of the sphere in focus, whereas in the case of the disc such longitudinal movement is not found to be required. Further, the luminous edge of the sphere is found to diminish in brightness much more rapidly than in the case of the disc when the observer's eye is moved laterally into the region of shadow. Similar differences are also found when we compare the diffraction into the region of shadow by a sharp straight edge and by the edge of a cylinder.

We recognise that the explanation we have offered is only qualitative. The reality of the effects described is, however, unquestionable, and we have no doubt that a quantitative explanation will be forthcoming when the diffraction problem is considered on the basis of the electromagnetic theory for the case of the large sphere. This problem has been handled by Poincaré, Nicholson, Macdonald, Bromwich, G. N. Watson and others. The Paper by Macdonald, on "The Diffraction of Electric Waves Round a Perfectly Reflecting Obstacle,"* might in particular be referred to, as the analysis contained in it approaches most closely to the point of view from which we have explained our experimental results. The formulæ given by Macdonald are, however, not in a form capable of immediate application to the problem without considerable labour. As the experimental work was completed last summer, and as we are at present engaged on other work, we have thought it best not to defer publication of the results any longer.

---

* Phil. Trans. R.S., A.210, 113 (1910). For other references *see* Bateman, "Electrical and Optical Wave Motion."

XXXV.—ON THE ABSORPTION AND SERIES SPECTRA OF NICKEL.

By Prof. A. L. NARAYAN, *D.Sc.*, *F.Inst.P.*, and K. R. RAO, *M.A.*

ABSTRACT.

The Paper gives an account of the experiments on the absorption spectrum of nickel by the under-water spark from λ6000-λ2000. In the region λ3800 to λ2100, 180 wavelengths were obtained in absorption. The majority of these lines were classified by Bechert and Sommer. Intensity values of the absorbed lines showed that the intensity rule and the selection rule for inner quantum numbers were accurately fulfilled. The results confirm in a striking manner the recent classifications of Bechert and Sommer in the arc spectrum of nickel.

ONE of the main approaches to the problem of atomic structure is by means of observations of absorption spectra of the vapours of the elements in the normal or excited states. According to Bohr's theory, for the vapour of an element to absorb lines corresponding to a given series in its spectrum, it is necessary that in the vapour there should be a fairly large number of atoms with orbits corresponding to the first term of the pulse of radiation to be absorbed. The position of the absorption spectrum is therefore of fundamental importance for the knowledge of the series scheme, as absorption lines, so far as they arise in non-luminous vapours, correspond to the unexcited natural state of the atom, the initial level of absorption being the "natural orbit" of the atom. The varieties of spectral series, their representation by formulæ and the possibility of other types of regularities in the arc and spark spectra of the different elements are subjects of far-reaching importance whose study, as Fowler put it, "bids fair to become the main avenue of approach to the problem of atomic structure."

In general, experimental arc and spark spectra of any particular element contain many lines in common; the enhanced lines are often excited in an ordinary electric arc and with greater prominence in the vacuum arc, while true arc lines (lines belonging to the neutral atom) appear in high-potential sources such as condensed sparks. According to Bohr's theory of spectra, arc and spark spectra are quite distinct, arc lines being emitted by the interorbital transitions of the valence electron in the neutral atom, while spark lines result in energy changes in atoms that have lost one or more of its outermost electrons. To provide data likely to be useful in identifying the series spectra of neutral atoms, the authors began two years ago a systematic study of the absorption of light by non-luminous vapours of different elements, by using a long column of vapour under purely thermal excitation, and the results of some of these are published in a number of Papers.(1) In view of the fact that most of the elements of the periodic table, particularly those of the higher groups, possess high boiling points, so that to obtain sufficient vapour for absorption experiments very high temperatures were necessary, absorption spectra of these elements were not studied till recently. But during the past few months, with the development of experimental technique, absorption spectra of a number of refractory elements were studied by McLennan, Zumstein, Angerer and Joos and others, as a result of which several lines have been classified.

In the identification of the regularities in the arc spectra, apart from the use of high-temperature furnace used by these authors, there is yet another means, particularly useful with metals having high boiling points. This method involves the use of high-frequency oscillatory spark under water between electrodes of the metal, and was in recent times used by Hulburt,(2) L. and E. Bloch,(3) Clark and Cohen(4) and others. In continuation of our experiments on absorption spectra we began recently an attack on the absorption spectra of the elements of the higher groups of the periodic table, particularly Fe, Co, and Ni, using the latter method. When experiments on Fe and Co were complete, Sur's Papers(5) giving an account of similar experiments appeared. Though in all these cases we studied the absorption to λ2000, while Sur went up to λ2400, our efforts were concentrated on nickel, and it is the purpose of the present Paper to give an account of the results of these experiments.

Angerer and Joos,(6) McLennan and McLay(7) and Buffam and Ireton(8) have also investigated the absorption spectrum of this element. McLennan and McLay with a furnace current of 40-45 amperes obtained 73 wavelengths in absorption, while Buffam and Ireton obtained 50 lines by the under-water spark method. As the accompanying tables and spectrograms show, about 180 wave-lengths were obtained in these experiments as absorption lines.

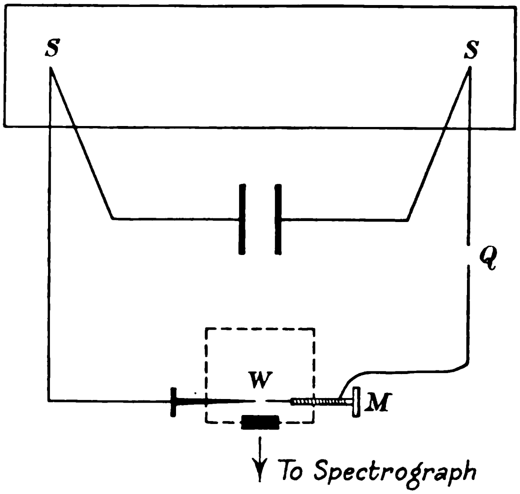


FIG. 1.

In connexion with this method of investigating the absorption and series spectra of an element, it is worth noting that if the spark is properly tuned it can be made to emit a perfectly continuous spectrum, which is of great advantage in absorption experiments. Appearance of absorption lines is favoured by increase of electrode diameter, increase of frequency and diminution of potential. When under these conditions the discharge passes, the discharge nucleus itself gives a continuous spectrum and is surrounded by a vapour mantle which contains mostly vapour particles in a normal state. Another peculiarity of the under-water discharge is that under these conditions it exhibits both emission and absorption lines, absorption lines belonging to the series systems in the arc spectrum, while emission lines mostly belong to the first spark spectrum. As will be seen from the note on the spectrum of Fe at the end, all the lines of the *DP* multiplet of the quartet system(9) of Fe^+ are exhibited as emission lines in the under-water spark spectrum of iron. This evidence is a sufficient proof that the under-water spark discharge is of great use in the study of the spectral structures for neutral and ionized elements.

EXPERIMENTAL.

Fig. 1 is a diagrammatic sketch of the electrical connexions for the spark under water. The secondary terminals *S*, *S* are connected to the under-water spark gap *W*, with an additional gap *Q* in series. The condenser capacity could be varied from 0·005 to 0·02 microfarad. The spark under water took place between pure-nickel rods, the distance between them being finely adjusted by a micrometer screw *M*.

In taking the photographs, a plane grating spectrograph was used for the region λ6000 to λ3400 and a large Hilger quartz spectrograph for the region λ3600-λ2000. For the region λ2400-λ2000 Hilger's Schumann plates were used. Up to λ2400 the best exposure was two or three minutes, while for the region of shorter wavelength the best exposure was found to be 15 to 20 minutes.

Recently Walters and Bechert and Sommer⁽¹⁰⁾ have classified a number of wavelengths in the arc spectrum of nickel. Bechert and Sommer have found that in this element the spectral terms are of odd multiplicity and found evidence for singlet, triplet and quintet systems and intercombinations. The fundamental term is an *f* term of the triplet system.

Owing to the diffuse nature of the lines in the absorption spectrum, attempts were not made to measure the wavelengths, but these were identified after a careful examination with the measures of Siegmund Hamm.⁽¹¹⁾ In the following table are given the wave-lengths (rounded off to the second decimal place), wave numbers and intensities (as obtained in absorption) of the absorption lines, together with the series notation by Bechert and Sommer :—

TABLE OF ABSORBED WAVE-LENGTHS.

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
		3858·28	3	25910·97	$\bar{D}_2{}^1-\bar{f}_3{}^{1a}$
		3807·14	1	26259·06	$\bar{D}_2{}^1-d_3{}^1$
		3783·52	0	422·94	$\bar{D}_2{}^1-\bar{f}_3{}^1$
		75·56	0	478·63	$D_2{}^1-d_2{}^1$
	3619·37	3619·39	7	27621·11	$D_2{}^1-\bar{F}_3{}^1$
		3612·73	2	672·03	$f_2{}^1-d_2{}^1$
	10·46	10·45	2	689·51	$\bar{d}_2{}^1-\bar{p}_2{}^1$
	3602·26	—	—	—	
	3597·71	3597·70	2	787·65	$d_1{}^1-\bar{p}_1{}^1$
		3571·87	3	989·54	$f_3{}^1-\bar{f}_3{}^{1a}$
3566·55	66·36	66·37	4	28031·71	$\bar{D}_2{}^1-D_2{}^1$
24·69	24·53	24·54	10	364·40	$d_3{}^1-\bar{p}_2{}^1$
		19·78	1	402·81	$f_2{}^1-\bar{f}_2{}^{1a}$
	15·06	15·06	7	440·93	$d_2{}^1-f_3{}^{1a}$
	10·37	10·34	6	479·16	$\bar{d}_1{}^1-\bar{p}_0{}^1$
	3500·87	3500·85	3	556·33	$f_3{}^1-d_2{}^1$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
3493·13	3492·96	3492·97	8	620·73	$\bar{d}_2^1-\bar{p}_1^1$
	83·83	83·78	3	696·31	$f_2^1-d_1^1$
	72·56	72·55	5	789·10	$\bar{d}_2^1-d_3^1$
61·84	61·65	61·66	8	879·63	$\bar{d}_3^1-\bar{f}_4^1$
	58·45	58·47	8	906·29	$\bar{d}_1^1-\bar{f}_2^{1a}$
	52·87	52·89	5	952·97	$\bar{d}_2^1-\bar{f}_3^1$
	3446·26	3446·26	7	29008·65	$\bar{d}_2^1-d_2^1$
	37·31	37·28	4	084·44	$f_4^1-\bar{f}_4^1$
	33·60	33·57	5	115·92	$\bar{d}_3^1-\bar{f}_3^{1a}$
	23·73	23·71	4	199·71	$\bar{d}_1^1-d_1^1$
	14·77	14·77	10	276·17	$\bar{d}_3^1-\bar{f}_4^{1a}$
		13·94	2	283·27	$\bar{d}_2^1-\bar{f}_2^1$
	13·52	13·48		287·26	$f_3^1-f_2^{1a}$
		09·58	0		$f_4^1-\bar{f}_2^{1a}$
3393·10	3392·96	3392·99	6	464·08	$\bar{d}_3^1-d_3^1$
	91·06	91·05	3	480·95	$f_4^1-\bar{f}_4^{1a}$
		89·36	1	495·68	
		86·95	0		
	80·57	80·58	7	572·29	$\bar{D}_2^1-\bar{P}_1^1$
	74·28	74·23	1	627·93	$\bar{d}_3^1-\bar{f}_3^1$
	72·05	72·00	1	647·55	
	69·57	69·58	7	668·83	$f_4^1-d_3^1$
	66·18	66·17	2	698·85	$f_3^1-F_3^1$
		65·77		702·31	$\bar{D}_2^1-\bar{f}_3^2$
	61·61	61·56	2	739·6	$\bar{d}_2^1-\bar{f}_2^{1a}$
		37·02	0		$\bar{d}_3^1-\bar{f}_2^1$
		28·72	0		$\bar{d}_2^1-d_1^1$
		22·32	1	30090·85	$\bar{D}_2^1-d_3^2$
	20·28	20·26	1	109·5	$f_3^1-D_2^1$
15·8	15·68	15·67	2	151·19	$\bar{d}_2^1-\bar{F}_3^1$
		3271·12	1		$\bar{d}_2^1-D_2^1$
		50·75	2	753·31	$D_2^1-d_2^2$
	3243·07	43·06	4	826·16	$\bar{d}_3^1-\bar{F}_3^1$
		34·66	1	906·31	
3233·05		33·17	1	920·5	
	32·93	32·95	5	922·66	
		26·99	1	979·69	
	25·06	25·03	2	998·53	$\bar{D}_2^1-d_1^2$
	21·68	21·66	2	31030·96	$f_4^1-\bar{F}_3^1$
3134·21	3134·09	3134·11	10	897·81	$\bar{d}_1^1-\bar{f}_2^2$
	14·14	14·13	1	32102·44	$d_2^1-\bar{P}_1^1$
		07·72	0	168·66	$f_3^1-d_3^2$
	05·48	05·47	1	191·97	$f_2^1-d_1^2$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
3102·02	01·87	01·88	10	229·18	$\overline{D}_2^{1}—\overline{F}_3^{2}$
	01·55	01·56		232·48	$\bar{d}_2^{1}—\bar{f}_3^{2}$
	3099·13	3099·12	1	32257·92	
	97·15	97·57	1	274·05	
		97·12		278·72	$f_3^{1}—f_2^{2}$
3080·9	80·79	80·76	2	450·15	$\bar{d}_1^{1}—d_2^{2}$
		66·46	0	601·47	
64·76	64·63	64·63	2	620·95	$\bar{d}_3^{1}—d_3^{2}$
57·79	57·64	57·65	9	695·41	$\bar{d}_1^{1}—d_1^{2}$
54·46	54·3	54·32	7	731·06	$\bar{d}_2^{1}—\bar{f}_2^{2}$
50·99	50·8	50·83	10	768·49	$\bar{d}_3^{1}—\bar{f}_4^{2}$
		45·01	1	831·08	$f_3^{1}—d_2^{2}$
38·09	37·92	37·94	8	907·5	$\bar{d}_3^{1}—\bar{f}_3^{2}$
		31·87	1	973·38	$f_4^{1}—\bar{f}_4^{2}$
	19·16	19·15	3	33112·29	$f_4^{1}—\bar{f}_3^{2}$
12·14	11·99	12·01	8	190·81	$\overline{D}_2^{1}—D_2^{2}$
03·76	03·58	03·63	10	283·39	$\bar{d}_2^{1}—d_2^{2}$
02·65	02·46	02·49	10	295·98	$d_3^{1}—d_3^{2}$
	2994·46	2994·46	3	385·31	
	92·59	92·60	3	406·07	$\overline{d_3^{1}}—\overline{f_2^{2}}$
		84·13	1	500·87	$f_4^{1}—d_3^{2}$
	81·68	81·65	2	528·7	$\bar{d}_2^{1}—d_1^{2}$
	43·95	43·92	4	958·39	$\bar{d}_3^{1}—d_2^{2}$
		2821·30	3	35434·29	$\bar{d}_3^{1}—\overline{F}_3^{2}$
		2798·65	4	720·99	$\bar{d}_2^{1}—D_2^{2}$
		2511·02	2	39812·46	
		10·89		814·61	
		2491·184	1	40129·45	
		90·689		137·43	
		84·039	1	244·87	$\overline{D}_2^{1}—o_3^{1}$
		76·88	1	361·25	$f_4^{1}—a_3^{1}$
		72·24	2		
2455·6		—			
		41·83	4	940·45	$\bar{d}_1^{1}—k_2^{1}$
37·98		37·90	3	41006·47	
29·17		—			
16·21		—			
		2424·03	4	241·16	$\bar{d}_1^{1}—m_2^{1}$
		23·66		247·39	
		23·33		253·02	$f_3^{1}—c_4^{1}$
		2421·23	4	41288·76	$f_3^{1}—e_4^{1}$
		19·31	5	321·52	$f_3^{1}—k_2^{1}$
2412·36		12·65	3	435·65	$f_3^{1}—l_3^{1}$
		01·85	8	621·95	$f_3^{1}—m_2^{1}$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
2396·74		2396·39	4	712·40	$f_2^1\text{—}u^1$
94·68		94·52	7	749·24	
		88·92	5	847·16	
87·87		87·56	4	871·05	$D_2^1\text{—}v^1$
		79·73	1		$\bar{D}_2^1\text{—}\bar{f}_2^3$
75·51		75·60	4	42081·77	
		75·43		084·83	
62·19		62·06	5	322·96	$f_3^1\text{—}o_3^1$
		60·64	5	348·48	$f_2^1\text{—}\bar{f}_3^3$
		58·87	5	380·3	$\bar{d}_3^1\text{—}c_4$
		56·87	5	416·18	$\bar{d}_3^1\text{—}e_4^1$
		55·06	5	42448·75	$\bar{d}_3^1\text{—}k_2^1$
	2347·47	—	—		
		46·64	6	601·23	$f_3^1\text{—}u^1$
		46·09	6	611·09	
45·48	45·47	45·55	6	621·04	$f_4^1\text{—}e_4^1$
41·30	—	—	—		
		38·5	9	749·4	$\bar{d}_3^1\text{—}m_3^1$
		37·82		761·84	$\bar{d}_1^1\text{—}t_3^1$
	37·52	37·49		767·90	$f_4^1\text{—}l_3^1$
	37·12	37·10		775·05	$\bar{d}_2^1\text{—}o_3^1$
34·68	—	—			
		31·70	3	873·98	$f_3^1\text{—}q_3^1$
	30·02	29·97	9	905·80	
25·91	25·82	25·80		982·77	$f_3^1\text{—}r^1$
		21·96	9	43053·93	$\bar{d}_3^1\text{—}\bar{f}_4^3$
	21·47	21·39		064·49	$f_2^1\text{—}v^1$
	20·11	20·03		089·60	$f_4^1\text{—}n_5^1$
18·60	18·80	18·78	9	112·91	
	17·14	17·16	9	143·06	$f_3^1\text{—}t_2^1$
		13·98	9	202·27	
	13·64	13·66		208·36	
12·50	12·35	12·34		232·99	$f_3^1\text{—}\bar{f}_3^3$
	11·01	10·96		258·81	$f_4^1\text{—}\bar{f}_4^3$
		2308·16	2	43311·19	
		07·35	2	326·37	$\bar{d}_2^1\text{—}q_3^1$
		06·42	2	343·90	
2302·56		02·97	4	408·75	
		01·57	10	435·25	$\bar{d}_2^1\text{—}r^1$
		00·77		450·24	$\bar{d}_3^1\text{—}o_3^1$
2296·66		2296·55	5	530·19	
		93·85	10	581·43	$d_2^1\text{—}t_3^1$
	2293·18	93·11		595·36	
	90·05	—	—	—	

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
75·79		75·57	1	931·41	
		74·65	2	949·14	$f_3^1 - v^1$
		71·94	3	44001·62	$\bar{a}_3^1 - q_3^1$
		70·21	2	035·21	
		67·55	5	086·8	$f_3^1 - f_2^3$
		66·40	5	109·15	
64·57	—	—	—	—	
		61·40	6	206·46	$f_4^1 - q_3^1$
		59·55	6	242·87	
58·2	—	58·13	6	270·62	$\bar{d}_3^1 - t_2^1$
		54·80	1	336·09	
		53·83	6	355·10	$\bar{d}_3^1 - \bar{f}_3^3$
		53·55	5	360·68	
53·0	—	—	—	—	
		51·47	4	401·67	$\bar{d}_2^1 - v^1$
47·3	—	—	—	—	
	44·53	44·50	8	540·21	$\bar{d}_2^1 - \bar{f}_2^3$
		30·93	2	810·35	
26·41	—	—	—	—	
		24·84	2	933·09	
		22·93	2	971·58	
	21·83	21·92	3	992·06	
		(2217·82)	4	45075·24	
16·52		16·46	4	102·93	
11·16		11·27 }	3	208·81	
		11·02 }	3	213·86	
		(2205·59)	1	325·15	
01·52		01·53	4	408·75	
		(2200·72)	4	425·45	
		2197·31	8	495·99	
2191·04	—	—	—	—	
		2190·18	2	644·05	
		2188*	8	45704·0	
		2186*	8	45731·0	
		2183*	6	45793·0	
2175·22	—	75·10	5	960·5	
		69·10	5	46008·6	
61·31	—	61·25	5	255·0	
59·83		59·80	5	286·1	
		57·84	3	328·0	
		2154*	7	46412·0	
		2142*	6	46670·0	
38·69		—	—	—	
		31·28	5	47013·5	
25·98		2126*		47022·0	
		24·84	3	047·6	
		21·4	2	123·8	

Wave-lengths marked * are probably unresolved lines clustered together into a broad band.

UNIV. OF MICH.

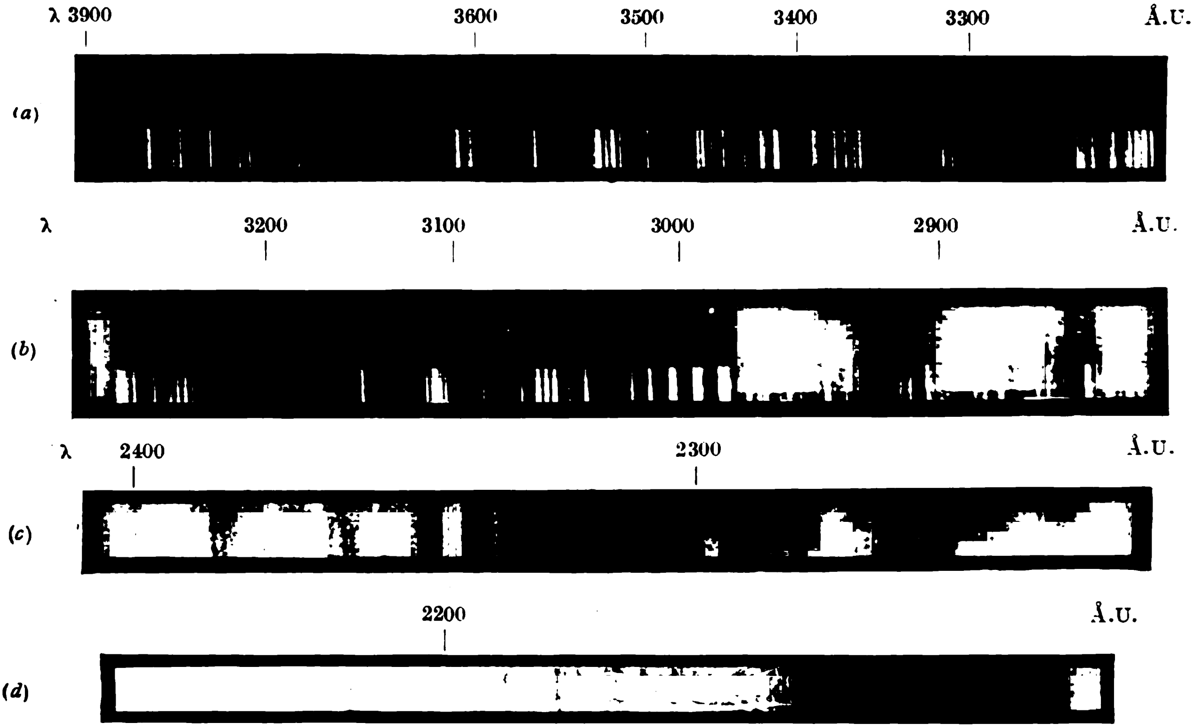


FIG. 2.—UNDER-WATER SPARK ABSORPTION SPECTRUM of NICKEL.

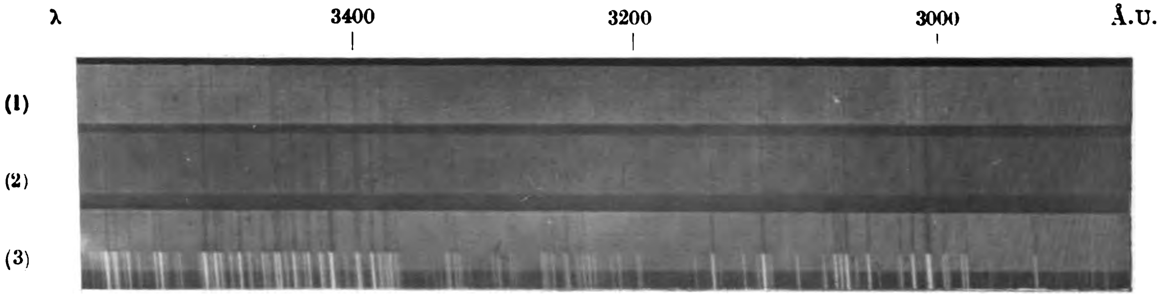


FIG. 3.—UNDER-WATER SPARK SPECTRUM of NICKEL.

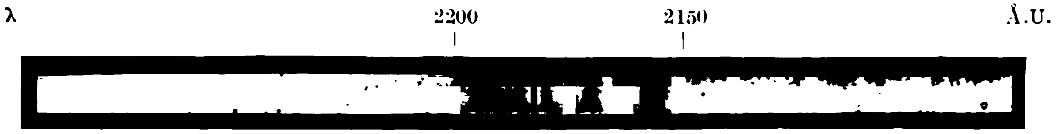


FIG. 4.—UNDER-WATER SPARK SPECTRUM of IRON.

[*To face page* 361.

A careful examination of the table shows that lines of multiplets having $\bar{d}^1$'s as initial orbits were obtained mostly as absorption lines. Furthermore, the results show that the intensity rule and the selection rule for the inner quantum numbers are accurately fulfilled. The presence of some absorption lines also indicates that the selection rule for azimuthal quantum numbers, however, breaks down. These may be ascribed to the strong electric and magnetic fields at the spark gap. Notable among these are the (f, f), (d, d), (d, D) combinations. It will also be found that wavelengths with u, v, t, o as the final level were mostly absorbed, while those with a and b as final levels were not absorbed.

Bechert and Sommer classified only lines up to λ2240. Of the 150 lines obtained in absorption by us in this region, 112 were classified by these authors. Between λ2240 and λ2100, 25 wavelengths were absorbed, many of these being intense in absorption, thereby showing that these also belong to some fundamental combinations. These experiments confirm in a striking manner the classification of Bechert and Sommer, though at the same time it must be remarked that many lines with the f term as the initial level were not obtained as absorption lines.

Fig. 3 shows the absorption spectrum of nickel from λ3600 to λ2900 under different conditions of excitation, which conclusively indicates that with proper arrangement the under-water spark can be made use of as an efficient means to the study of the absorption and series spectra of different elements, particularly those with high boiling points.

NOTE ON Fe SPECTRUM.

The arc spectrum of nickel is exactly similar to that of iron, which consists of triplets, quintets and septets, with intercombinations among the different systems. The under-water absorption spectrum of this element was found to consist of some very strong lines in the region λ2300-λ2100 which were not included in Laporte's(12) scheme. The following table gives the wave-lengths of these lines.

TABLE OF ABSORBED WAVE-LENGTHS (Fe).

λ	Int.	λ	Int.
2191·95	10	2162·10	
91·2		61·69	
		61·28	
87·29		60·23	
86·90	10	56·91	
		55·95	
86·49		55·78	10
		55·14	
81·60	10	50·66	
80·92		50·26	
		48·57	
78·14	10	47·84	
76·92		47·14	
66·92	10	44·57	
66·68		41·83	
		31·04	

As was already indicated, the under-water spark spectrum of Fe exhibited some emission lines belonging to the first spark spectrum of iron, prominent among these being the lines of the *DP* multiplet of the quartet system of Fe^+.

MULTIPLET IN THE SPECTRUM OF Fe^+.

	D_4^4	436·51	D_3^4	288·50	D_2^4	166·23	D_1^4
P_3^4	5 2562·541 39011·94		4 2591·549 38575·43		2 2611·08 38286·91		—
422·3							
P_2^4	—		4 2563·484 38997·73		4 2582·590 38709·24		1 2593·528 38543·03
236·34							
P_1^4	—		—		3 2566·916 38945·6		3 2577·92 38779·35

REFERENCES.

(1) Narayan and others : Proc. Roy. Soc., 106, p. 51, 596 (1924) ; Phil. Mag., Vol. 1, p. 645 (1925).

(2) Hulburt : Phys. Rev., Aug. (1924).

(3) L. and E. Bloch : J. de Phys., p. 309 (1922).

(4) Clark and Cohen : Trans. Roy. Soc. Can., 20, Sec. 3 (1926).

(5) Sur : Phil. Mag., Feb., 433, 451 (1926).

(6) Angerer and Joos : Ann. d. Phys., 74, 8 (1924).

(7) McLennan and McLay : Trans. R.S.C., 3, p. 89 (1925).

(8) Buffam and Ireton : Trans. R.S.C., 3, p. 113 (1925).

(9) Meggers and others : J.O.S.A. and R.S.I., 9, p. 371 (1924).

(10) Bechert and Sommer : Ann. d. Phys., Aug. (1925).

(11) Siegmund Hamm : Z. wiss. Photogr., 13, 105 (1913).

(12) Laporte : Z.S. f. Phys., 23, 135 (1925), and 26, 1 (1924).

XXXVI.—THE INFLUENCE OF ELECTROLYTES IN ELECTRO-ENDOSMOSIS.

By H. C. HEPBURN, *B.Sc.*, Research Student in Physics at Birkbeck College, London.

(*Communicated by* Prof. A. GRIFFITHS.)

ABSTRACT.

This Paper gives the results of electro-endosmotic determinations with certain aqueous solutions of electrolytes in glass diaphragms, and values are obtained for the interfacial potential of the Helmholtz electrical double layer. The dependence of the conductivity on the electro-endosmotic flow has been investigated by measurements of the current flowing through the diaphragm during each determination, and the data used to trace the variations in the thickness and the charge of the electrical double layer by the application of a formula derived by Smoluchowski.

INTRODUCTION.

NUMEROUS researches have been undertaken in recent years on electro-endosmosis, cataphoresis, and stream potentials with aqueous solutions of electrolytes against solids (and certain oils), which become negatively charged in pure water. The results have usually been given in terms of the potential ζ of the electrical double layer, which, according to the Helmholtz theory, is set up at the interface solid (or oil)-aqueous solution. A general conclusion to be drawn from these results, as Freundlich* has observed, is that with most electrolytes with univalent, inorganic cations, ζ increases initially with the concentration, attains a maximum value, and then strongly and regularly decreases.

The data for the interface glass-aqueous solution, however, is not altogether in harmony with this conclusion. Kruyt† investigated the stream potentials produced by pumping aqueous solutions of hydrochloric acid, potassium chloride, and barium chloride through glass capillaries, and obtained pronounced maxima in the ζ-concentration curves in all the cases mentioned, including that of barium chloride. On the other hand, Elissafoff‡ and Powis§ in electro-endosmotic measurements with aqueous solutions of sodium chloride (Elissafoff), potassium chloride (Powis), and barium chloride (Elissafoff and Powis) against glass, found that increase in the electrolyte concentration, with the most dilute solutions, produced a decrease in the value of ζ. Kruyt† has questioned the method used in the calculation of Elissafoff's results, but without being able to reconcile the data for glass capillaries with his own results.

The present work, consisting of direct electro-endosmotic measurements with aqueous solutions in glass diaphragms, is devoted to the study of the phenomenon at low electrolyte concentrations, with special reference to the production of maxima in the ζ-concentration curves. At the same time, the dependence of the conductivity on the electro-endosmotic flow has been investigated, and the data used to trace the variations in the thickness and the charge of the electrical double layer by the application of a formula derived by Smoluchowski.||

---

* "Kapillarchemie," p. 351 (1922).

† Koll. Zeit., 22, 81 (1918); *see* also Freundlich and Rona, Sitz. d. Preusz. Akad. d. Wiss, 20, 397 (1920).

‡ Zeit. Phys. Chem., 79, 385 (1912).

§ Ibid., 89, 91 (1915).

|| Anz. Akad. Wiss Krakau, A, 182 (1903).

THE APPARATUS.

The apparatus employed, the main parts of which were made from hard glass tubing, was similar in construction to that used by Briggs, Bennett and Pierson* but it was found desirable to adopt a different arrangement of electrodes, and a somewhat different mode of procedure.

The horizontal electrolyzing chamber *A*, *A'* (Fig. 1), with vertical side arms *S*, *S'*, was enlarged slightly between *D* and *D'*, to form a chamber in which the porous diaphragm was built up. The side arms *S*, *S'* were fitted with grooved corks, which carried the electrodes *E*, *E'*. Attached to the horizontal chamber by ground glass joints were the three-way taps *T*, *T'*, which, in turn, were connected, by means of short rubber connexions, to the bent tube *BHB'* of uniform bore. The speed and direction of flow through the diaphragm were measured by the movement of a small air bubble (*H*), introduced into the tube *BHB'* by manipulation of the taps *T*, *T'*.

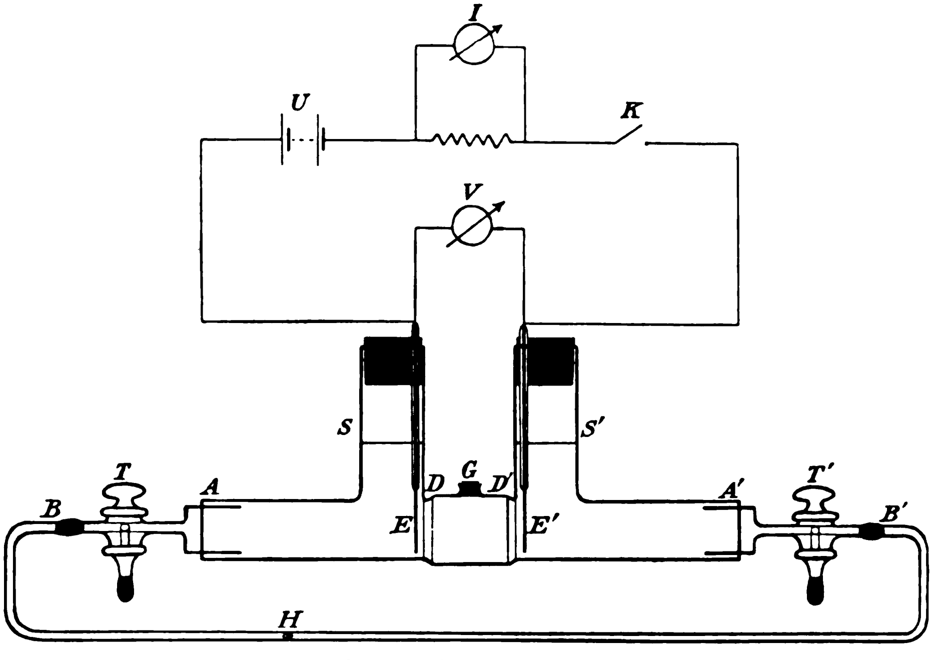


FIG. 1.—THE APPARATUS.

The capacity of the tube *BHB'* was determined as follows :—

Connexion was made with the chamber *AA'* at *T*, and liquid delivered from the tube in drops at the tap *T'*. The liquid delivered from *T'* while the bubble moved over 25 cm. of the tube was collected and weighed, the results of several determinations giving the capacity of the tube as 1·836 c.c. per 25 cm. length.

Pure vaseline was employed as a lubricant for the taps and joints, and the outsides were smeared with a mixture of vaseline and paraffin wax ; the taps, in addition, were fitted with small rubber stoppers during the determinations of liquid flow.

---

* Jour. Phys. Chem., 22, 256 (1918).

THE DIAPHRAGM.

The diaphragm material, in the form of a 200 mesh powder, consisted of an easily fusible glass, similar to that constituting the capillaries used in the stream potential experiments of Freundlich and Rona.* After careful grading, the powder was heated first with strong hydrochloric acid; then, after washing with distilled water, with chromo-sulphuric acid; and finally washed thoroughly with distilled water. The purified glass was kept sealed under distilled water.

Immediately before building up each diaphragm a suitable quantity of the purified powder was placed in a U-tube with distilled water, and 200 volts applied between the electrodes in the limbs; this operation was repeated with changes of water until no further electrolysis could be detected. The electrolyzing chamber *A A'* was then fixed in a vertical position, and the diaphragm built up in the section *D D'* on a perforated cork, upon which was placed a compact plug of glass wool, which had previously been treated in the same manner as the glass powder. The glass powder, suspended in distilled water, was poured on to the plug, and the water drawn through with the aid of a filter pump. Finally, the diaphragm was completed by adding an upper plug of glass wool. Guiding lines 5 cm. apart were provided at *D* and *D'*, so that each diaphragm, including plugs, could be constructed of this length.

THE ELECTRODES.

A silver anode and a silver chloride cathode, prepared after the manner recommended by Washburn,† were employed. For the anode, about 35 cm. of silver wire 1 mm. in diameter was cemented into a thin glass tube. The protruding length, constituting the greater part of the wire, was wound into the form of a flat spiral and plunged into warm dilute nitric acid until violently attacked; washed with boiling distilled water, and then with alcohol, the excess of which was finally removed by the application of heat. The tube carrying the electrode was then fixed in the grooved cork of the side arm *S'* of the apparatus, so as to bring the plane of the spiral normal to the axis of the electrolyzing chamber *A A'*. A similar spiral of silver wire, upon which a layer of granular silver chloride had been deposited electrically from a molar solution of sodium chloride, was employed as cathode, and suspended in the side arm *S* of the apparatus. With electrodes of this type it was found possible to obtain results at much lower voltages than were applied by Briggs, Bennett and Pierson.‡

The current meter *I*, fitted with a variable shunt so as to obtain a wide range, and the battery of storage cells *U*, were placed in series with the electrodes through the key *K*, and the high-resistance voltmeter *V* placed across the electrodes. In determining the current through the diaphragm, adjustment was made in respect of the current (generally small in relation to the main current) through the voltmeter.

EXPERIMENTAL.

A separate diaphragm was prepared for each solution studied, but the same quantity of purified glass powder was used in each case, and each diaphragm built up under similar conditions. In addition, new electrodes were prepared for use with each diaphragm. The special method employed for washing out the diaphragm permitted the use of the same diaphragm for different concentrations of a particular solution.

Before building up each diaphragm, the whole apparatus was thoroughly washed out with hot chromo-sulphuric acid to remove grease and other impurities. Traces of impurities in the tube *BHB'* were found to impede the progress of the air bubble index ; but this trouble was entirely removed by the cleansing treatment with chromo-sulphuric acid.

---

* Loc. cit.

† Jour. Am. Chem. Soc., 31, 322 (1909).

‡ Loc. cit.

Determinations of the flow were made first with conductivity water, and then with the particular solution in increasing concentration up to 0·005 molar.

The method adopted for washing out the diaphragm was as follows :—

The bubble tube *B'HB* was cut off from the electrolyzing chamber by means of the taps *T*, *T'*, and the chamber emptied of liquid. The solution of next higher concentration was then introduced with a head of liquid in the side tube *S*. Under the influence of the hydrostatic pressure the solution flowed through the diaphragm into the right-hand part of the chamber, the flow being maintained by drawing solution from the tap *T'* at convenient intervals, and adding to the solution in the side arm *S*. After a considerable amount of solution had flowed through the diaphragm the chamber was emptied, and the operation repeated with a head of liquid in the side arm *S'*. After four such washings, with liquid heads alternately in each side arm, the liquid in the tube *BHB'* was siphoned out and replaced by conductivity water, and a small air bubble introduced by manipulation of the taps *T*, *T'*. Control experiments showed that similar washings, with a further quantity of solution, produced no appreciable alteration in the results.

After the apparatus had been allowed to stand for about thirty minutes, the tube *BHB'* was connected with the chamber *AA'*, and the bubble timed over 5 cm. of the tube with the aid of a stop watch, readings of current and applied potential difference being taken at the same time.

The temperature of the room in which the work was undertaken was maintained as far as possible constant at 18°C., determinations being made when the solution in the apparatus attained this temperature. Control experiments, with a thermometer in the side tube *G* of the chamber *AA'*, showed that there was no appreciable temperature rise in the diaphragm during each determination.

RESULTS.

(*a*) *Preliminary.*

Table I gives the results of a series of measurements with conductivity water at various applied potentials.

TABLE I.

V	T	$I/TV \times 10^4$
8·24	299·0	4·06
12·34	200·8	4·04
16·48	150·4	4·03
20·62	119·7	4·05
Volts	Secs.	

V is the potential difference applied at the electrodes, and T the time of flow over 5 cm. of the bubble tube. It will be seen from column 3 that the values give an accurate linear relation between the electro-endosmotic flow (proportional to I/T), and the total fall in potential through the diaphragm (proportional in this case to the applied potential) in agreement with previous experimental work* and with the theory of Helmholtz and others.†

---

* *See* the historical account by T. R. Briggs, Jour. Phys. Chem., 21, 198 (1917).

† *See* part (*b*) of this Section.

Table II, relating to solutions of potassium chloride, records the results of experiments designed to give the relation between the applied potential difference and the total fall in potential through the diaphragm.

TABLE II.

c	V	I_e	T	$I_e/TV \times 10^3$
0·0002	8·12	5·40	93·0	7·15
	8·12	5·60	97·0	7·11
	8·12	5·80	99·6	7·17
0·002	8·12	5·40	60·4	11·01
	8·12	5·60	62·5	11·04
	8·12	5·80	65·2	10·96
Mols. per litre	Volts	Cm.	Secs.	

For this purpose the electrodes were set with the aid of a travelling microscope at effective distances of 2, 3 and 4 mm. respectively, from the extremities of the diaphragm, allowance being made for the thickness of the wire constituting the electrodes; and the applied voltage (V), time of flow (T) over 5 cm. of the bubble tube, and the distance (I_e) between the electrodes, taken in each case. It will be observed from column 5 that the values of I_e/TV are practically the same, at a given concentration (c in Table), for all three positions of the electrodes. Since the electro-endosmotic flow, at a given concentration, is proportional to the potential gradient in the diaphragm, it appears from this result that the total fall in potential (E) through the diaphragm, when the electrodes are placed close to its extremities, is given, within a fraction of 1 per cent., by VI_d/I_e, where I_d is the length of the diaphragm.

In order to test whether placing the electrodes close to the ends of the diaphragm introduced disturbances in the flow and the current by reason of concentration changes about the electrodes, a series of observations was carried out with potassium chloride solutions over the concentration range 0·0002 molar to 0·005 molar, with the electrodes at an effective distance of 4 mm. from the extremities of the diaphragm. In each case the bubble was timed over a section of the tube, allowed to run over the next section, and then timed over the third section.

TABLE III.

c	E	T	I
0·0	7·17	296·5	84
	7·17	295·1	80
0·0002	7·17	96·3	282
	7·17	96·8	291
0·0005	7·17	68·0	497
	7·17	66·8	493
0·0007	7·17	59·1	677
	7·17	59·4	677
0·001	7·17	57·2	867
	7·17	56·8	875
0·002	7·17	62·9	1,420
	7·17	61·7	1,420
0·005	7·17	223·6*	3,090
	7·17	214·8*	3,090
Mols. per litre.	Volts.	Secs.	Micro-amperes.

* Bubble timed over 2½ cm. only of the tube.

The results are given in Table III, and show that the variation in the time of flow for each pair of observations was generally under 1 per cent. with concentrations up to 0·001 molar, about 2 per cent. for 0·002 molar, and about 4 per cent. for 0·005 molar, the current (*I* in Table, column 4) in each case remaining remarkably steady. Compared with the results of previous investigators, these differences are not very considerable, but the final observations in the present work (*see* Table IV) were each repeated after washing out the diaphragm with fresh solution.

(*b*) *Determinations of Interfacial Potential.*

Table IV and the graphs of Fig. 2 give the results for aqueous solutions of potassium chloride, barium chloride and hydrochloric acid.

TABLE IV.

(1) Potassium chloride.					(3) Hydrochloric acid (with conductivity water).				
c	E	T	ζ	Mean ζ	c	E	T	ζ	Mean ζ
0·0	7·17	303·5	0·048		0·0	7·17	299·3	0·049	
	7·17	299·9	0·048	0·048		7·17	297·4	0·049	0·049
0·0002	7·17	96·9	0·150		0·0002	7·17	86·5	0·169	
	7·17	98·1	0·148	0·149		7·17	87·4	0·167	0·168
0·0005	7·17	68·8	0·211		0·0005	7·17	60·1	0·243	
	7·17	68·2	0·213	0·212		7·17	59·7	0·245	0·244
0·0007	7·17	60·7	0·239		0·0007	7·10	54·7	0·270	
	7·17	60·1	0·242	0·241		7·10	55·1	0·268	0·269
0·001	7·17	57·9	0·251		0·001	7·10	54·3	0·272	
	7·17	57·9	0·251	0·251		7·10	54·7	0·270	0·271
0·002	7·17	63·9	0·228		0·002	7·10	72·7	0·203	
	7·17	63·3	0·230	0·229		7·10	72·2	0·205	0·204
0·005	7·17	223·8*	0·065		0·005	7·10	249·4*	0·059	
	7·17	224·6*	0·065	0·065		7·10	251·2*	0·059	0·059
(2) Barium chloride.					(4) Hydrochloric acid (with distilled water).				
c	E	T	ζ	Mean ζ	c	E	T	ζ	Mean ζ
0·0	7·10	294·0	0·050		0·0	7·10	86·7	0·169	
	7·10	295·9	0·050	0·050		7·10	85·8	0·171	0·170
0·0002	7·10	115·6	0·128		0·0002	7·10	65·4	0·225	
	7·10	114·5	0·129	0·128		7·10	66·0	0·223	0·224
0·0005	7·10	103·0	0·143		0·0005	7·10	60·0	0·245	
	7·10	103·3	0·143	0·143		7·10	59·5	0·247	0·246
0·0007	7·10	106·7	0·138		0·0007	7·10	54·9	0·268	
	7·10	105·8	0·139	0·139		7·10	54·6	0·269	0·268
0·001	7·10	118·5	0·124		0·001	7·10	54·3	0·270	
	7·10	119·2	0·124	0·124		7·10	54·5	0·270	0·270
0·002	7·10	163·1	0·090		0·002	7·10	72·6	0·202	
	7·10	164·7	0·090	0·090		7·10	72·1	0·204	0·203
0·005	7·10	459·8*	0·032		0·005	7·10	251·8*	0·058	
	7·10	462·4*	0·032	0·032		7·10	252·6*	0·058	0·058
Mols. per litre.	Volts.	Secs.	Volts.	Volts.	Mols. per litre.	Volts.	Secs.	Volts.	Volts.

* Bubble timed over 2½ cm. only of the tube.

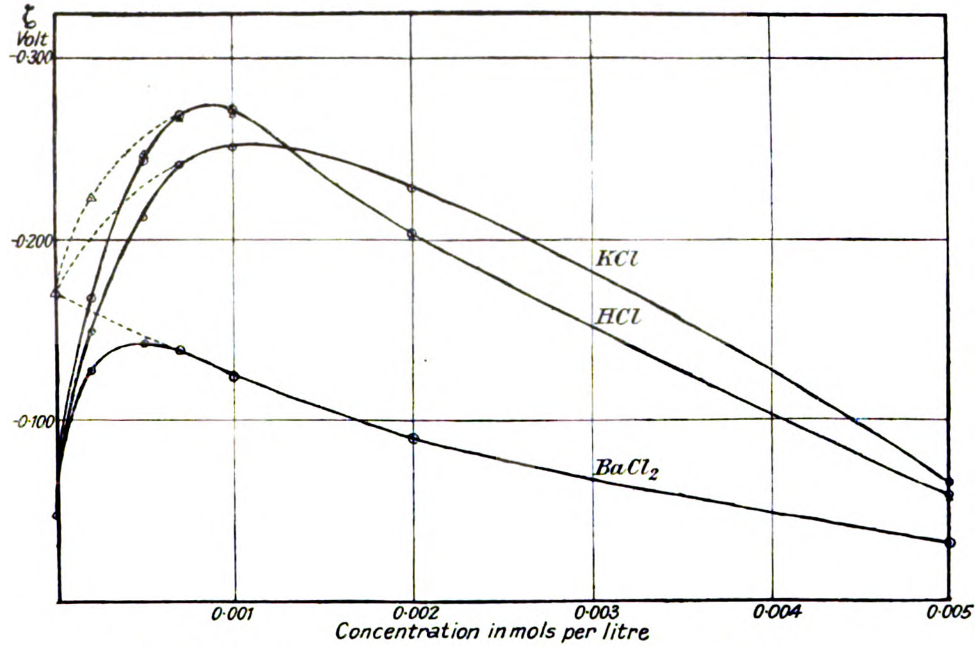


FIG. 2.—VARIATION IN THE POTENTIAL OF THE DOUBLE LAYER.

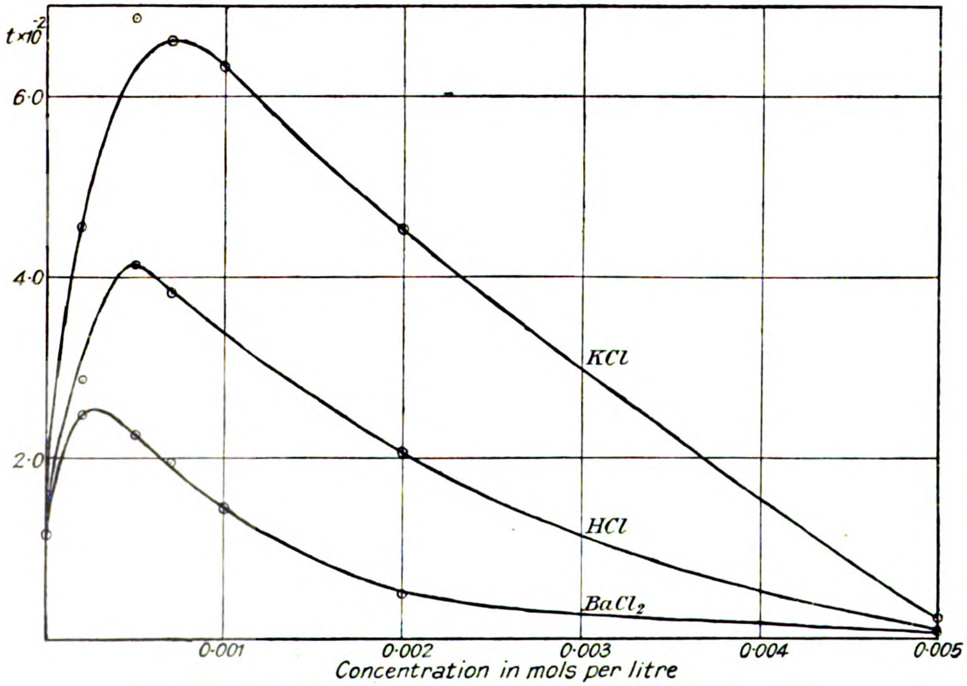


FIG. 3.—VARIATION IN THE THICKNESS OF THE DOUBLE LAYER.

ζ (column 5, Table IV.) is the potential of the electrical double layer at the interface glass-aqueous solution, calculated from the formula

$$v = q\zeta ED/4\pi\eta I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where v is the amount of liquid transported in unit time through the diaphragm, E the total fall in potential through the diaphragm, D the dielectric constant, η the viscosity coefficient of the liquid, and q and I respectively the effective cross-section and length of the diaphragm. ζ is negative in sign throughout.

Smoluchowski* has shown mathematically that expression (1), which is similar in form to that derived by Helmholtz† for a single capillary, is valid for the case of a porous diaphragm. The expression differs from that of Helmholtz, however, in containing the dielectric constant D. The inclusion of this factor follows the modern view‡ that the two layers forming the double layer do not lie, as assumed by Helmholtz, at a distance of one molecular diameter from one another, but extend much more deeply into the liquid. Gouy§ has shown that a diffuse double layer of this character may be replaced by two parallel sheets of charge—i.e., by a double layer of the form conceived by Helmholtz. The values calculated by Gouy (e.g., 9·6$\mu\mu$ for 0·001 molar solution) for the thickness of this equivalent, Helmholtz double layer are quite small in relation to the radius of a capillary of 0·05 mm. bore, which is roughly equivalent to a single channel in the present diaphragms, so that the condition imposed by Helmholtz, in deriving the expression for ζ, that the thickness of the double layer should be negligible in comparison with the dimensions of the cross section of the tube, may still be regarded as satisfied.

The values for q/I (*see* Table V) were obtained by means of a method due to Fairbrother and Mastin.||

TABLE V.

$N/10$	$\lambda \times 10^3$	E	$I \times 10^3$	q/I $(I/\lambda E)$	Mean q/I
KCl	11·20	7·17	42·34	0·527	
		3·59	21·12	0·525	0·526
$BaCl_2$	9·08	7·10	33·80	0·524	
		3·55	16·88	0·524	0·524
HCl_A	35·14	3·55	65·4	0·524	
		3·55	65·1	0·522	0·523
HCl_B	35·14	3·55	65·6	0·526	
		3·55	65·6	0·526	0·526
	Recip. Ohms.	Volts.	Amps.		

Each series of observations was concluded with a determination using $N/10$ solution. No perceptible liquid transport was observed at this concentration, but readings of the current and applied potential difference were taken as before. No electro-endosmotic flow being observed, the surface conductivity in $N/10$ solution (*see* part (*c*) of this Section) was assumed to be negligible in relation to the bulk conductivity ; consequently, with current I, total fall in potential through the diaphragm E,

---

* Loc. cit.

† Wied. Ann., 7, 337 (1879).

‡ *See* Freundlich, "Kapillarchemie," pp. 342-3 (1922).

§ Jour. d. Phys. (4), 9, 457 (1910).

|| Jour. Chem. Soc., 125, 2319 (1924).

and q and I respectively, the effective cross-section and length of the diaphragm, the following relation obtained,

$$I=E\lambda q/I \text{ or } q/I=I/\lambda E,$$

λ being the specific conductivity of the solution employed. The values of λ were obtained mainly from the data of Kohlrausch.*

With the extremely dilute solutions of the present work, the dielectric constant and the viscosity coefficient are practically the same as for pure water, and the values 80 and 0·01057, relating respectively to the dielectric constant and the viscosity coefficient of pure water, have been used throughout in applying the formula for ζ.

The results of sections (1) to (3) of Table IV refer to solutions made up with freshly-prepared conductivity water of specific conductivity approx. 10^{-6} recip. ohms. Section (4) of Table IV gives a series of results with solutions of hydrochloric acid prepared with laboratory distilled water (specific conductivity approx. 8×10^{-6} recip. ohms).

(*c*) *Dependence of the Conductivity on the Electro-endosmotic Flow and Variation in the Thickness of the Electrical Double Layer.*

The results are given in Table VI.

TABLE VI.

	c	$\lambda\times10^5$	I	i_q $(E\lambda q/I)$	i_w $(I-i_q)$	i_w/i_q	$t\times10^{-2}$	$\zeta/t\times10^4$
(1) Potassium Chloride	0·0	0·10	78·8	3·8	75·0	19·7	1·17	4·09
	0·0002	2·57	281·2	96·9	184·3	1·902	4·55	3·28
	0·0005	6·40	487·2	241·4	245·8	1·018	6·88	3·07
	0·0007	8·94	668	337	331	0·982	6·62	3·64
	0·001	12·73	856	480	376	0·783	6·32	3·97
	0·002	25·25	1,389	952	437	0·459	4·52	5·06
	0·005	62·17	3,058	2,345	713	0·303	0·22	29·0
(2) Barium Chloride	0·0	0·10	75·8	3·7	72·1	19·5	1·28	3·90
	0·0002	4·70	419·6	174·9	244·7	1·399	2·49	5·14
	0·0005	11·56	768	430	338	0·786	2·25	6·35
	0·0007	16·13	966	600	366	0·610	1·96	7·08
	0·001	23·10	1,257	859	398	0·463	1·44	8·63
	0·002	44·84	2,268	1,668	600	0·360	0·50	17·9
	0·005	106·7	4,546	3,970	576	0·145	0·07	48·4
(3) Hydrochloric acid	0·0	0·10	79·8	3·8	76·0	20·0	1·20	4·07
	0·0002	7·56	651·6	283·5	368·1	1·298	2·87	5·84
	0·0005	18·85	1,244	707	537	0·760	4·16	5·87
	0·0007	26·36	1,683	979	704	0·719	3·82	7·05
	0·001	37·59	2,008	1,396	612	0·438	4·46 3·40†	 7·97
	0·002	75·06	3,537	2,787	750	0·270	2·05	9·94
	0·005	186·3	8,170	6,918	1,252	0·181	0·10	57·1
	Mols. per litre	Recip. Ohms.	Micro-amperes					

---

* *See* Noyes and Falk, Jour. Am. Chem. Soc., 34, 454 (1912).

† Interpolated value from the graph in Fig. 3.

In column 3 of the Table the mean total current (I) flowing through the diaphragm, as measured during each determination of electro-endosmotic flow, is given, and in column 4, the voltaic current (i_q), calculated from the expression $E\lambda q/I$, the letters having the significance indicated in the previous section.

In order to verify that this expression for the voltaic current could be applied in the present work, control experiments were carried out to ascertain (1) whether the electrolyte concentration in the diaphragm differed materially from the bulk concentration, by reason of adsorption phenomena attending the formation of the electrical double layer, and (2) whether the movement of the solution in the diaphragm altered the voltaic current.

To test the first point, a quantity of the purified glass powder was carefully dried, placed in a bottle, and 0·0002 molar potassium chloride solution added to fill the bottle. The bottle was then sealed and agitated vigorously to bring the whole of the solution into contact with the powder. After the bottle had been allowed to stand for about thirty minutes, the supernatant liquid was decanted off, a further quantity of solution added, and the operation repeated. Finally, after three such washings, the contents of the bottle were carefully filtered through glass wool to remove suspended glass particles, and the conductivity of the filtrate determined. Before proceeding to the filtration, a quantity of the original solution was poured through the filter, so as to minimise the possibility of adsorption of the solute taking place during the filtration. The results obtained were found to agree (within 1-2 per cent.) with concurrent determinations of the conductivity of the original solution, and also with the value given by the data of Kohlrausch. A further quantity of the dried powder was then taken, and the shaking process repeated with several washings of 0·002 molar potassium chloride solution. Conductivity measurements with the filtrate in the latter case gave similar agreement with the results for the original 0·002 molar solution. These results indicate that the final equilibrium concentration in the diaphragm, after several washings with a particular solution, was practically the same as the bulk concentration.

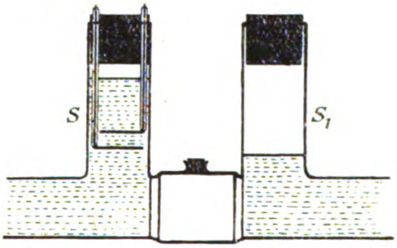


FIG. 4.—DETERMINATION OF CONDUCTIVITY WITH SOLUTION FLOWING PAST THE ELECTRODES.

To test the second point, the original apparatus was employed with the bubble tube cut off from the chamber AA'. The electrodes were fixed in the vertical side arm S of the apparatus with the spirals one above the other, after the manner of the electrodes in a conductivity cell (Fig. 4). The current was first measured with the solution in the two side arms S, S' at the same level, the solution between the electrodes consequently remaining at rest. Solution was then withdrawn from the side arm S' by means of the tap T', giving a head of liquid in the arm S, which produced a flow through the diaphragm and movement of the solution between the electrodes. The head of liquid in the arm S was arranged so that the average rate of flow past the electrodes was of the same order as the flow through the diaphragm in the electro-endosmotic determinations described in the previous section. Within a fraction of 1 per cent. no alteration in the current was observed. It appears from this result that the voltaic current through the diaphragm in the electro-endosmotic determinations, was not perceptibly different from that which would have been obtained if the solution had been at rest.

Values of the surface current (i_w), given by ($I - i_q$) are scheduled in column 5 of Table VI, and values of i_w/i_q in column 6.

In column 7 of the table, values are given of the expression $\frac{\zeta^2}{\lambda i_w/i_q} \times 10^{-2}$, which, as indicated by an expression derived by Smoluchowski* is proportional to the thickness of the electrical double layer. The values of ζ are taken from Table IV.

Smoluchowski's formula relates to the case of a single capillary, and is as follows,

$$\frac{i_w}{i_q} = \frac{\omega}{q\eta\delta\lambda}\left(\frac{\zeta D}{4\pi}\right)^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

ω is the circumference of the tube, δ the thickness of the electrical double layer, and the other letters have the significance indicated in the previous section. This expression, suitably modified as regards the constants q and ω, has been used in connexion with the work of Stock† on powdered quartz. In the range of electrolyte concentration of the present work the expression reduces to the form $i_w/i_q = \zeta^2/\delta\lambda \times$ (a constant), giving δ proportional to $\frac{\zeta^2}{\lambda i_w/i_q}$, the expression t of column 7 of Table VI. The variation of t with the concentration is shown graphically in Fig. 3.

DISCUSSION OF RESULTS.

The curves of Fig. 2 show that the potential of the interface glass-aqueous solution increased initially with the concentration, attained a maximum value, and then regularly decreased with solutions of potassium chloride, barium chloride and hydrochloric acid, in agreement with Kruyt's general result. The curves are similar in shape to those of Kruyt, and in the same relative positions; but the values of ζ are generally greater than those obtained by him, and the maxima occur at higher concentrations—e.g., maximum value of ζ in the present work with potassium chloride solutions $-0{\cdot}251$ volts at a concentration of 0·001 molar, and in Kruyt's work $-0{\cdot}086$ volts at 0·0003 molar. In making the comparison, it should be observed that Kruyt calculated the values of ζ in absolute units from the original stream potential formula of Helmholtz‡ and the values given in his Paper consequently require to be multiplied by 300/80 to obtain ζ in volts and to correct for the dielectric constant.

The values of ζ for the interface glass-pure water are in good agreement with those obtained from the results of the experiments of Quincke and Tereschin§

---

* Loc. cit.

† Anz. Akad. Wiss. Krakau, A, 635 (1912); and *see* Freundlich, "Kapillarchemie," p. 338 (1922).

‡ Loc. cit.

§ *See* Freundlich, "Kapillarchemie," p. 330 (1922).

on the rise of liquid in capillary tubes under the influence of an applied potential; the values also fall between those (−0·035 and −0·089 volts respectively) given by the data of Kruyt and Powis (loc. cit.).

The importance of employing water of a high degree of purity in electro-endosmotic determinations is shown from the results of sections (3) and (4) of Table IV. The value of ζ with distilled water (specific conductivity 8×10^{-6} recip. ohms) is −0·170 volts, against −0·049 volts with conductivity water (specific conductivity 10^{-6} recip. ohms); the values of ζ for the distilled water solutions of hydrochloric acid are similarly greater than those for the conductivity water solutions, as indicated by the dotted curve in Fig. 2; above 0·0007 molar concentration, however, the results with distilled water and conductivity water practically coincide. A parallel to this result is given by the work of Alty* on the cataphoresis of gas bubbles in water. Alty found that the velocity of cataphoresis increased with the conductivity of the water to a maximum value in water of specific conductivity $8{\cdot}5\times10^{-6}$ recip. ohms. The dotted curves in Fig. 2 for solutions of potassium chloride and barium chloride are obtained by taking the value of ζ at zero concentration as −0·170 volts, and combining this result with the values for conductivity water solutions of concentration greater than 0·0007 molar. It will be seen that the maximum with barium chloride disappears entirely.

The results of Table VI, columns 3-6, given graphically in Fig. 5, are in agreement with the conclusions of Smoluchowski, from theoretical considerations, that electro-endosmosis must increase the ordinary galvanic conductivity in consequence of the surface current produced. The values given in column 6 for the ratio of the surface current to the voltaic current show that the surface current with pure water was practically twenty times as great as the voltaic current. The values for the solutions are much smaller, the greatest being 1·902 (with 0·0002 molar potassium chloride), and decrease with rising concentration. In previous work on this subject,† conductivity cells have apparently been used, with the space between the electrodes filled with the diaphragm material and the experimental liquid; and the conductivity determined by the usual alternating-current method of Kohlrausch. Stock observed the phenomenon with several organic liquids in quartz powders, and found that the current strength, with the finest quartz particles, increased to approximately twenty times the ordinary galvanic value. Fairbrother worked with an 80 mesh Jena "Gerate" glass powder and various aqueous solutions of electrolytes. The values for i_w/i_q given by his work, with solutions of potassium chloride and hydrochloric acid, are considerably smaller than those of Table VI; but the variety of glass employed was different from that of the present work, and it is possible that the conditions obtaining in electro-endosmotic experiments, where the liquid is allowed to flow freely through the diaphragm, may not have been reproduced with the diaphragm and solution confined in a conductivity cell.

The relation between the interfacial potential ζ and the charge σ per unit surface of each face of the electrical double layer‡ is given by the expression

$$\zeta=4\pi\sigma\delta/D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where δ is the thickness of the electrical double layer and D the dielectric constant.

---

* Proc. Roy. Soc., 106, 315 (1924).

† *See* Stock, loc. cit., and Fairbrother, Jour. Chem. Soc., 125, 2495 (1924).

‡ *See* Freundlich, "Kapillarchemie," p. 329 (1922).

It follows, for a given value of σ, that ζ varies with the thickness of the double layer. There appears to be practically no experimental data in regard to the dependence of δ on the concentration of the solution, but the conclusions of Gouy* on theoretical grounds, as Freundlich† has pointed out, are opposed to the possibility that the rising branches of the ζ-concentration curves of Fig. 2 are to be attributed to increase in the thickness of the double layer. It appears from the graphs of Fig. 3 (and Table VI), however, that the thickness of the double layer increased initially with the concentration, attained a maximum value, and then regularly decreased with each of the three solutions studied; and, further, the curves of Figs. 2 and 3 are in the same relative positions with the exception of the rising branches for the solutions of hydrochloric acid. The maxima in the curves of Fig. 3, however, occur at somewhat lower concentrations than those in the curves of Fig. 2.

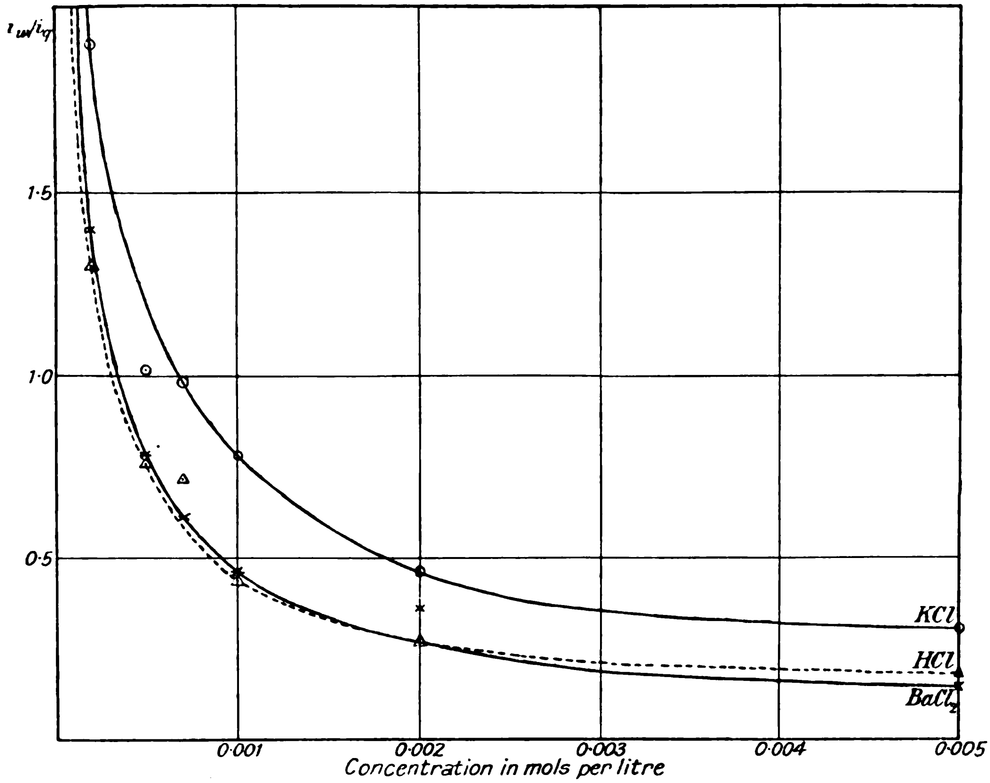


FIG. 5.—DEPENDENCE OF THE CONDUCTIVITY ON THE ELECTRO-ENDOSMOTIC FLOW.

It follows from equation (3) that, within the range of concentration of the present work, σ, the charge per unit surface of each face of the electrical double layer, is proportional to ζ/δ, and therefore to ζ/t, where t is given by $\frac{\zeta^2}{\lambda i_w/i_q}$ (see p. 373). Values of $\zeta/t \times 10^4$, calculated from the data in Tables IV and VI, are given in column 8 of Table VI. The result follows that the negative charge per unit surface of the wall layer in pure water actually increased with the concentration over the whole range of observations with solutions of barium chloride and hydrochloric acid; with solutions of potassium chloride the negative charge increased with the concentration from 0·0005 molar onwards.

---

* Loc. cit.

† "Kapillarchemie," p. 352 (1922).

In regard to the physical significance of the results for δ and σ, it is pointed out that these quantities are not directly connected with the actual distribution of charges in the neighbourhood of the wall, but relate to the Helmholtz electrical double layer which Gouy* has shown to be equivalent to such a distribution.

SUMMARY OF RESULTS.

(1) The results indicate that the potential (ζ) of the interface glass-aqueous solution increases initially with the concentration, attains a maximum value, and then regularly decreases with solutions of hydrochloric acid, potassium chloride and barium chloride, in agreement with the general result of Kruyt in stream potential determinations.

(2) Higher values of ζ at concentration below 0·0007 molar were obtained when the solutions were prepared with laboratory distilled water (specific conductivity 8×10^{-6} recip. ohms), instead of with conductivity water (specific conductivity 10^{-6} recip. ohms), indicating, in the case of solutions of barium chloride, entire disappearance of the maximum in the ζ-concentration curve. This result indicates the importance of employing water of a high degree of purity in electro-endosmotic determinations.

(3) Measurements of the current flowing through the diaphragm during each determination of electro-endosmotic flow give results in harmony with the conclusions of Smoluchowski, from theoretical considerations, that electro-endosmosis must increase the ordinary galvanic conductivity in consequence of the surface current produced.

(4) The application of the formula derived by Smoluchowski to the data under (1) and (3) indicates that the thickness of the electrical double layer also reaches a maximum with increasing concentration in the case of each of the three solutions studied.

(5) The data for ζ and for the thickness of the electrical double layer lead to the result that the negative charge per unit surface of the wall layer against glass increases with the concentration up to 0·005 molar (the highest concentration of the present work) with solutions of hydrochloric acid and barium chloride; with solutions of potassium chloride the charge increases with the concentration from 0·0005 molar onwards.

So far as a search of the literature has been made, this Paper records one of the first systematic attempts to investigate experimentally the dependence of the thickness and the charge of the electrical double layer on the electrolyte concentration of the solution.

The author wishes to express his thanks to Professor Albert Griffiths for the interest he has taken in this investigation.

---

* Loc. cit.

DISCUSSION.

Mr. F. E. **Smith** said that the Paper was of considerable interest, and the results appeared to have been obtained with great care. The author's glass powder diaphragm had worked satisfactorily, but personally, in using a similar diaphragm with $AgNO_3$ as the electrolyte, he had experienced the difficulty that with currents above a certain strength silver becomes deposited on the glass, and thereafter the greater part of the current passes through the metallic silver instead of through the liquid. This phenomenon of electrostenolysis had been very little investigated, and he recommended it to the author's attention.

Prof. A. **Griffiths** said that the author had made some useful improvements in the experimental method, and on the theoretical side had shown the intimate relation between the P.D. across the double layer and the thickness of the latter. He had originally suggested that the author should take up this subject, because he had experienced certain difficulties in diffusion experiments which might possibly be accounted for by electro-endosmosis. In the diffusion apparatus employed water flowed very slowly through a long capillary tube into a wide chamber, and then again through a capillary tube. Whenever the water in the chamber was taken out and replaced the viscous resistance to the flow of the water was unaccountably increased for a time, and it seemed possible that potential differences of concentration of the solute in different regions of the tubes might set up electro-endosmotic effects which would account for the phenomenon. Prof. Griffiths had obtained a good deal of light on the question from the author, and hoped that the latter would extend the investigation.

Dr. H. **Borns** asked why glass was selected for the diaphragm. For experiments of this kind the diaphragm should be chemically indifferent, but this could not be the case with glass. Powdered quartz or carborundum might be used, but even these substances might not be quite unexceptionable.

Mr. R. P. **Fuge** asked whether the cylinders on either side of the diaphragm were open to the atmosphere. Otherwise a difference of pressure might arise which would affect the results obtained.

Dr. D. **Owen** asked which of the variables occurring in the author's fundamental equation were measured directly, and which represented hypothetical quantities.

Author's reply: In reply to Dr. Borns, glass was selected for the diaphragm so as to obtain electro-endosmotic data for comparison with the results of Kruyt and others in stream-potential determinations with glass capillaries. In the view of Freundlich,* the slight solubility of the glass is an important factor in the formation of the electrical double layer.

In regard to Mr. Fuge's inquiry, the corks carrying the electrodes were provided with grooves, so that the cylinders on either side of the diaphragm were open to the atmosphere.

In reply to Dr. Owen, and as indicated in the Paper, all the variables occurring in the fundamental equation must be regarded as representing hypothetical quantities in so far as they are not directly connected with the distribution of charges in the neighbourhood of the diaphragm wall, but relate to the Helmholtz electrical double layer which Gouy has shown to be equivalent to such a distribution. The values given in the Paper as relating to the quantities mentioned are derived from direct measurements (*a*) of the liquid flow; (*b*) of the applied potential; and (*c*) of the current flowing through the diaphragm.

It is interesting to note, in connexion with the point raised by Dr. Owen, that Miss Laing and McBain† have recently proposed a migration theory of electro-kinetic phenomena in which an endeavour is made to avoid the use of hypothetical quantities. The work of Miss Laing with solutions of sodium oleate lends support to the views put forward, but further experimental verification would appear to be necessary before the theory can be regarded as definitely established.

---

* "Kapillarchemie," p. 347 (1922).

† Jour. Phys. Chem., 28, 673 (1924); Ibid., 28, 706 (1924).

XXXVII.—THE LATENT HEAT OF FUSION OF SOME METALS.

By J. H. AWBERY, *B.A.*, *B.Sc.*, and EZER GRIFFITHS, *D.Sc.*

Received April 28, 1926.

ABSTRACT.

The latent heats of a number of the commoner metals have been measured by determining the total heat of liquid and solid from a series of initial high temperatures.

The calorimetry was by the method of mixtures, introducing several refinements, of which the chief were the use of fairly large charges of metal (of the order of 2 kilograms), and a device by which the hot charge was not allowed in contact with the water of the calorimeter until the latter was completely closed ; this eliminates error due to production and escape of steam, with a consequent loss of heat. The device referred to consisted in the provision of a sheet metal vessel suspended by threads from the main lid of the calorimeter. The aperture through which the charge was introduced was closed by a rotating lid, in the main lid, and the crucible being introduced, was submerged after the closing of this smaller lid by means of a wire passing through an eyelet in the base of the calorimeter, and out at the top.

The results for the latent heat are given below :—

Metal.	Melting point, °C.	Latent Heat. (Calories per gm.)
Aluminium	657	92·4
Antimony	630	24·3
Bismuth	269	13·0
Lead	327	6·2$_6$
Magnesium	644	46·5
Tin...	232	14·6
Zinc	420	26·6

The Paper also contains values for the specific heats up to the melting point, obtained by differentiation of the temperature-total heat curves.

INTRODUCTION.

THE primary object of the investigation recorded in this Paper was the determination of the latent heat of fusion of the commoner metals. Although many workers have studied this problem in the past, the published data reveal astonishing discrepancies. Aluminium, for example, has had the values below ascribed to this physical constant.

Latent Heat of Aluminium.

Date.	Observer.	Latent Heat calories per gram.
1886	Pionchon	80
1904	Glaser	77
1911	Greenwood	93
1914	Lascento	64
1919	Wüst	94

In other cases, such as those of antimony and magnesium, we have been unable to find any recorded values. It was, therefore, decided to undertake experimental work, with a view to determining the latent heat of the following metals :—

Aluminium, Antimony, Bismuth, Lead, Magnesium, Tin and Zinc.

It has also been possible to determine the mean specific heats of these metals over a range of temperature.

Review of Previous Work.

Researches on the thermal capacity of metals at high temperatures have occupied the attention of many workers in the past 100 years, so it is desirable to give a sketch of their methods before describing new work.

Historically, one of the earliest workers was Rudberg,(1) who in 1830 determined the latent heat of lead, his value 5·86 comparing very well with the more recent determinations. He employed the method of cooling and, by comparing the rates of cooling of the metals whose thermal constants were unknown with that of mercury, which was assumed, he deduced the latent heats.

Person's(2) work dates back to 1848. He employed a calorimetric method and in the case of lead worked with specimens weighing 680 grams. The fusion points of the metals were determined by mercury thermometers, the glass of which was "cristal de Choisy-le-Roi." He corrected the readings of these thermometers to the scale of the gas thermometer by means of Regnault's table.

The Table below shows how his values of latent heats and of the fusion points compare with those obtained by us :—

Metal.	Latent Heat. Person.	Latent Heat. A. & G.	Melting Point (Person). Hg. therm.	Melting Point (Person). Air therm.	Melting Point (Present day values).
Tin	14·252	14·6	235·0°	232·7°	232
Bismuth ...	12·640	13·0	270·5°	266·8°	269
Lead ...	5·369	$6{\cdot}2_6$	334·0°	326·2°	327
Zinc ...	28·13	26·6	433·3°	415·3°	418

Spring(3) in 1886 investigated a series of tin lead alloys and in the course of these experiments determined the latent heats of fusion of tin and lead.

Pionchon,(4) a pupil of Berthelot, also carried out investigations about 1886 by the usual calorimetric method of mixtures.

Attention might be drawn to his method of measuring temperatures. He adopted Violle's method in which a small ingot of platinum was heated alongside the specimen and dropped into water. His temperature scale read about 50°C. low at 950°C.

Richards(5) (Chem. News, 68, 1893) criticizes Pionchon's value and states that the total heat of liquid aluminium at its melting point is 258·2, instead of the value 239·4, given by Pionchon.

Heycock and Neville(6) in 1897 found the latent heat of fusion of zinc by an indirect method. They made observations of the depression of the freezing point on adding a second metal and of the absolute temperature of the freezing point of the alloy. They then calculated the latent heat from the formula

$$\delta\theta = 0{\cdot}0198\ \theta^2/L$$

where $\delta\theta$ is the atomic depression of the freezing point and θ the absolute temperature of the freezing point. They found

$$\delta\theta = 5{\cdot}11$$

Hence L for Zinc=28·33 cals.

In 1903 Robertson,(7) at the conclusion of a Paper dealing with another subject, states that he has determined calorimetrically the latent heats of several metals. In the absence of detail it is impossible to assess the value of his results.

Harker and Greenwood(8) (1905) employed the calorimetric method with one notable modification. The metal sheathed in silica was dropped, not directly into the calorimeter water, but into a funnel-shaped brass tube filled with calcined precipitated hydrate of magnesia, which formed a very light powder.

The object of the device was to prevent the splashing of the water which occurred if the metal was dropped in directly. The device had, however, the drawback that it retarded the attainment of temperature equilibrium between the metal and the water.

Guinchant(9) (1907), in a very brief Paper without illustrations, describes some experiments on the latent heat of silver nitrate by the usual calorimetric method, and mentions an electrical method by which he determined the latent heat of tin and obtained the value 14·3. He employed a silvered Dewar vessel surrounded by a thick layer of asbestos paper and by metallic reflecting shields. At the bottom of the vessel was placed an electric heater. The material to be studied occupied 30 c.cs. and was placed within the heater.

He determined the heat loss by a separate experiment in which the electrical energy required to maintain a series of steady temperatures was measured.

Mazzotto(10) in 1910 adopted the "cooling curve" method. He was investigating the lead tin alloys and in the course of the research determined the latent heats of these two metals.

In 1913 he published a further Paper(11) dealing with the tin cadmium series.

G. D. Roos(12) (1916) obtained the latent heats of magnesium and aluminium by a somewhat involved process. He made a comparison of the cooling curves of these metals with those of metals of known latent heat under identical conditions of experiment, reducing the observations by a method proposed by Tammann. The procedure followed was to plot the rate of cooling against the time. The latent heat is given by the equation $mR=C\Delta Zf(V)$,

where m is mass of metal,
R its latent heat,
C a constant,
ΔZ the duration of freeze,
$f(V)$ a function of the rate of cooling at the maximum, which corresponds to the rate of cooling just after the completion of the freeze.

The form of the function $f(V)$ was determined by utilizing the values quoted in Table below :—

Metal.	Latent Heat.	Observer.
Tin	14·25	Person
	14·65	Spring
	13·6	Mazzotto
	14·05	Robertson
Bismuth	12·4	Mazzotto
	12·64	Person
Cadmium	13·7	Person
Lead	5·32	Spring
	5·37	Person
	5·37	Mazzotto
	6·45	Robertson
Zinc	28·0	Mazzotto
	28·1	Robertson

It might be remarked here that the values in the above Tables were by no means representative of the data known at that time. For example, in the Table of values for tin the values given by Glaser(13) (1904), Wüst(14) (1919), Guinchant(9) (1907) have been ignored. Again, in the case of zinc the values of Heycock and Neville,(6) Lascento,(15) Greenwood,(8) and Glaser(13) were omitted. These range from 26·0 to 29·9.

Taking the latent heat of Cadmium as unknown, Roos calculated it from the value of each of the other four metals separately, assuming $f(V)$ to be of the form V^n and trying various values for n. The value of n which gave the best agreement for the latent heat values of Cadmium deduced from the various known latent heat values of the other metals was assumed to be the correct one.

Calculated Value of the Latent Heat of Cadmium.

Comparison Metal.	$n=2{\cdot}0$	$n=2{\cdot}1$	$n=2{\cdot}2$	$n=2{\cdot}3$
Zn	14·3	13·97	13·62	13·3
Pb	13·6	13·63	13·71	13·8
Bi	13·2	13·50	13·73	14·0
Sn	13·3	13·58	13·82	14·1

The most consistent values are obtained by taking $n=2{\cdot}2$.

The defect of this procedure is that the resulting value is subject to considerable uncertainty if the latent heat values of the comparison metals are not absolutely correct. He assumes the same value for n over a temperature range from 430°C. to 660°C. His value for aluminium is 80, whereas the value found in the present investigation was 92·4.

Roos checked this indirect method by a direct calorimetric determination of the total heat of specimens of liquid magnesium and liquid aluminium sealed in quartz tubes when cooling from 700°C. down to room temperature. To obtain the latent heat from this total heat, it was necessary to subtract the heat given up by the liquid in cooling through an interval of 50° and that given up by the solid in cooling from the freezing point down to the temperature of the calorimeter.

The total heat of the solid was deduced by extrapolating other observers' values for the specific heat and that of the liquid was deduced from that of the solid, together with the latent heat, by means of Tammann's rule

$$\frac{L}{T}=C_1-C_2$$

where L is the latent heat,
T is the absolute temperature of the melting point,
C_1 and C_2 the specific heats of the liquid and solid respectively. The agreement was remarkable.

Aluminium 80 by the cooling method
82 ,, ,, calorimetric method.
Magnesium 70 by the cooling method,
72 ,, ,, calorimetric method.

It is difficult to understand why he did not measure the total heat in the solid state up to the freezing point.

Wüst, Meuthen, and Durrer(14) (1918) employed an apparatus based on that of Oberhoffer. It was a combination of the ice calorimeter and vacuum furnace. For temperatures below 1,300°C. a nichrome-wound furnace was employed, while for higher temperatures a carbon spiral furnace was substituted. With this furnace a temperature of 1,600°C. could be reached in 3 minutes. This rapid raising of the temperature was necessary because with a slower rate of heating the walls of the glass enclosure became too hot.

The metal specimen was contained in a fused silica envelope, the ratio of the weight of the silica to that of the metal being from one-half to one-fifth, but as the specific heat of silica is about fivefold that of tin and lead, the correction for the heat capacity of the envelope became of serious magnitude in these experiments. The use of the ice calorimeter sets a limit to the size of specimen which can be manipulated conveniently. The use of small-sized specimens in calorimetry at high temperatures is not to be recommended, as the heat loss in the transference period becomes of serious magnitude. The experiments appear to have been carried out with care and thoroughness, but their values differ markedly from those of other observers.

White(16) has made the following criticisms of Wüst's methods :—

" His furnace was in a highly exhausted tube, which extended down into an ice calorimeter. The solid metals were ordinarily used bare, but were enclosed in silica glass when they were to be melted. Comparisons with the three solid metals, silver, gold, copper, up to 900° or 1,000° showed no difference, due to enclosure, in the specific heat so observed. The furnace thermel—i.e., thermo-electric thermometer—which was, as in our work, alongside the specimen, was found to be at the same temperature. In these special tests, as in most of the regular observations, the agreement was usually to 1 per cent. The tests and agreements reported are thus entirely favourable.

" The furnace, however, was entirely open at the bottom, which presumably caused much greater temperature difference through radiation than there were in our carefully-partitioned furnace. The high vacuum should have greatly diminished conduction and convection of heat, leaving heat transfer dependent on radiation. This evidently has a tendency to make the temperatures of enclosed bodies depend more on that of distant objects and on possibly variable radiating power. In Wüst's calorimeter the specimen fell into a metal box with a sheet nickel lid, which, still surrounded by vacuum, rested in a glass tube. The heat transfer was thus probably almost entirely by solid contact and radiation, and would, therefore, tend to vary with slight changes in the lie of the specimens or in the character of their surfaces, causing variations in the amount of heat escaping upward. In our case the specimen was dropped at once under water, and most of the heat transfer was over in the first minute. Wüst's agreement with the work of others is not very good. For the six metals, aluminium, chromium, cobalt, copper, nickel and silver, he differs in every case by from 4 per cent. to 8 per cent. at 100 deg. from Tilden or Schübel, who usually agree with each other to 1 per cent. At 500 deg. Wüst's discrepancy is less, but compared with specially accurate determinations in the Geophysical Laboratory, his value for silica glass, though high at 100 deg., is 5 per cent. too low at 900 deg. He agrees to 2 per cent. or better with our value for platinum from 200 to 1,400 deg."

Iro Iitaka(17) (1919) has carried out an investigation into the variation of the specific heat up to the melting point and the heat of fusion of some metals. He employed the method of mixtures with water or aniline as calorimetric liquid, the latter liquid being used to avoid explosion when the metal introduced was molten. The specimen was always fitted in a quartz vessel, and by making blank experiments with the empty container the loss of heat in the transit from the furnace to the calorimeter was allowed for. The water equivalent of the calorimeter was determined by dropping pure lead heated to 250° C. into the calorimeter. Four experiments gave the values 14, 14, 15, 15 (mean 14·5). Calculation of the water equivalent from the weight of copper, glass, etc., gave the value 13. It is stated that the temperature of the specimen was assumed to be uniform and in equilibrium with the thermoelement if the latter remained constant for about 10 minutes.

The results finally quoted by Iitaka take into account the values given by previous workers: the effect of this procedure has been generally to raise the values above the values actually found in his own experiments.

Walter P. White(16) (1921) has described experiments on the latent heats of fusion of two metals, nickel and monel metal, which have not been studied in the investigation described in this Paper. Specimens weighing about 27 grams were contained in closed silica glass tubes. The weight of metal was about 27 grams and the weight of the silica sheath 8·5 grams. The work was carried out with all the refinements of technique of this experienced investigator, and the only point of criticism is the small weight of material experimented with.

The results were checked by pouring directly into the calorimeter, nickel just ready to solidify, and agreement to about 2 per cent. with the furnace method was obtained.

In the present investigation the " method of mixtures " was employed, as this offered the simplest solution of the main problem, namely, the determination of the latent heats. It might be mentioned in passing that an electrical method was also tried. In this the metal was maintained in the solid state at an initial temperature which was very little below its melting point, and then the amount of electrical energy required to raise it to a temperature slightly above the melting point was determined by measuring the watts dissipated in a heating coil immersed in the metal.

The results obtained by the electrical method for the one metal tried—lead—were in good agreement with those obtained by the " method of mixtures." The " method of mixtures " has inherent limitations when it is desired to measure the variation of the specific heats of metals with temperature, and it is probable that the electrical method will ultimately be developed for this.

Two practical difficulties are encountered when applying the " method of mixtures " to high-temperature measurements:—

(1) Heat loss in the transfer of the metal from the furnace to the calorimeter.

(2) The formation of steam when the hot metal strikes the water.

As regards the first, various expedients have been tried to minimise the error due to the cooling during the transfer.

For example, the furnace may be mounted directly over the calorimeter and the crucible dropped right through into the water in the calorimeter. The difficulty which then arises is elimination of the heat transfer from the furnace to the calorimeter, especially when it is opened directly over the calorimeter.

In the present series of experiments the error due to heat loss in transfer was largely diminished by a different procedure. A considerable quantity of metal was used (of the order of a hundredfold that employed by previous investigators), and the furnace was mounted alongside the calorimeter jacket but well shielded from it. The advantage of this procedure is obvious, doubling the dimensions of the specimen increases the heat capacity eightfold, whilst the heat loss in transfer, being proportional to the area, is only multiplied fourfold.

Similarly, the actual calorimetry is simplified, since a large weight of water may be used without the temperature rise becoming too small to be measured accurately. Consequently, in all these experiments samples ranging in weight from 4 lb. for aluminium to 7 lb. for lead were used.

The second practical objection to the method of mixtures was overcome by the use of a simple device for completely enclosing the hot charge in the calorimeter before the water had access to it. Consequently when it actually came into contact with the water the steam formed could not escape from the calorimeter.

We may now consider the experimental arrangements in detail.

The Furnace was an electrical resistance furnace sufficiently deep to provide a length of about 8 ins. over which the temperature was fairly uniform.

The Crucible, of iron or graphite, was supported in the uniform-temperature region of the furnace in such a manner that it could be transferred rapidly to the calorimeter.

The temperature of the test specimen was measured by a thermoelement enclosed in a sheath and well immersed in the molten metal or in a hole drilled in the solid metal.

A crucible was always used, whether the metal was in the solid or liquid condition, for the reason stated in the discussion of the " heat loss in transfer."

When working with metals which did not attack iron, crucibles of this material were used, as they had the advantage of low thermal capacity. For the other metals graphite crucibles were adopted, as this material was found to be well suited to working with oxidisable metals.

The thermal capacity of the crucibles was determined by making " blank " experiments in which the empty crucible was heated up and transferred in a similar manner to that followed in the main experiment.

The Thermocouple for Measuring the Temperature of the Heated Metal.—A platinum, platinum rhodium thermoelement was used. Before the experiment it was calibrated by intercomparison with standards whose temperature-E.M.F. curves had been determined by the following fixed points :—

Sulphur	Boiling point.	444·5°C.
Antimony	Freeze point.	630°C.
Sodium Chloride	,,	801°C.
Gold	,,	1,063°C.
Copper	,,	1,083°C.

After the completion of the series of experiments the calibration of the thermo-element was checked at the freezing point of salt (Na Cl), and the boiling points of water and sulphur. The original calibration was confirmed by these checks.

The temperature of the metal in the furnace was read to an order of accuracy of 0·5°C. An uncertainty of 0·5°C. in the temperature of the molten metal would not cause an error of more than $\frac{1}{4}$ per cent. in the latent heat determination in the most unfavourable case of the metal with the lowest melting point, bismuth.

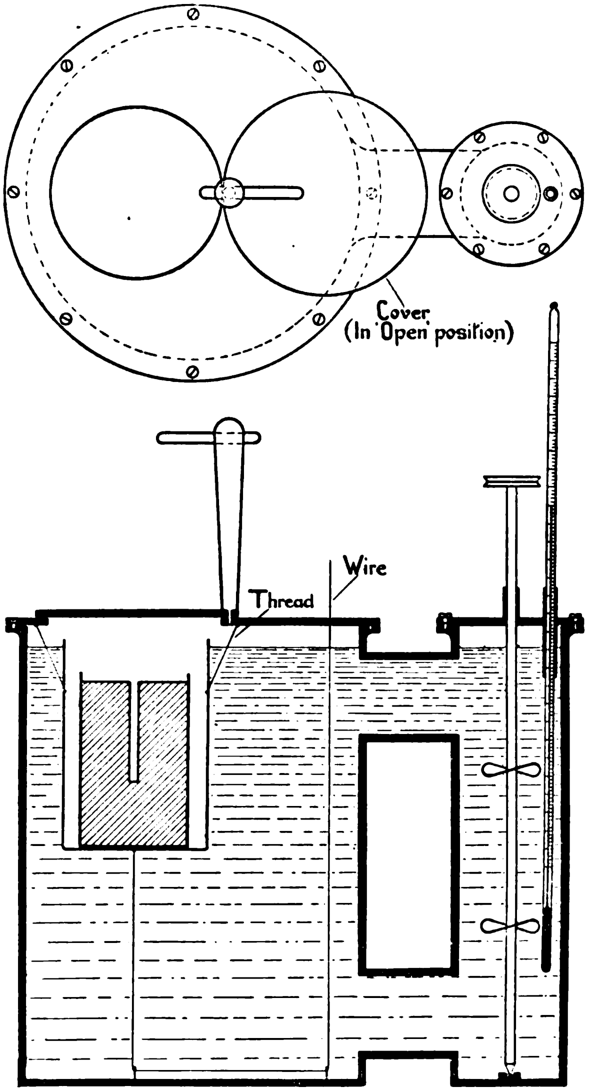


FIG. 1.

The Calorimeter.—This was of the form shown in Fig. 1, which shows a section (with the lid closed) and a plan (lid open). The main vessel was 12 in. in diameter by 19 in. in depth. The dimensions were so proportioned that the average temperature rise of the water on dropping in the heated metal would be about 5°C. or 6°C.

Thorough mixing of the water in such a vessel is important, and the method adopted by us will be seen in Fig. 1. Alongside the main calorimeter is a smaller vessel, 4 in. in diameter, connected to it by two wide pipes. The stirrer consists of two propellers on a shaft running the length of this chamber, and rotated by an electric motor. The blades of the propeller are so inclined that the water in the smaller chamber is lifted and thrown through the upper pipe into the large chamber. The thermometer is inserted through the tube seen projecting through the top of the small chamber.

The main vessel of the calorimeter was closed by a heavy cover with a 5 in. hole bored in it. This hole could be closed quickly by a well-fitting rotating lid, the secondary lid being manipulated by a wooden handle projecting up out of the enclosure. Reference has already been made to the desirability of preventing the escape of steam when the hot metal is plunged into the calorimeter. The device employed to overcome this was very simple and effective. A sheet metal vessel was suspended by three threads from the top of the calorimeter with the open mouth just above the surface of the water. The crucible was placed in this vessel in the first place, and the second lid of the calorimeter closed quickly. The vessel was then drawn down under the water surface by means of a wire attached to its base, and passing through eyelets in the bottom of the calorimeter.

With this arrangement any steam formed could not escape, as the calorimeter was completely closed before the water came into contact with the hot metal. It was, of course, essential that both calorimeter lids should make good thermal contact with the body of the calorimeter. A film of Russian tallow was found to answer quite satisfactorily, as the rubbing surfaces had been machined true.

The calorimeter was constructed entirely of copper, with a small amount of solder for the joints. The water equivalent of the calorimeter was calculated from the weight of copper and the specific heat, and was about 1,820 gram calories. The quantity of water worked with was about 28 litres, hence an error of 1 per cent. in the assumed value of the specific heat of copper would imply an error of 0·06 per cent. in the latent heat values.

The Calorimetric Thermometers.—For the various ranges of temperature covered in the investigation, two thermometers were employed. One divided directly into hundredths of a degree between 13 and 20°C., and the other, used only in experiments with large temperature rises, divided into tenths. With the former thermometer readings could be taken to 1/500 of a degree, and with the latter to 1/100 of a degree.

To avoid parallax error, a lens was used for reading the thermometers. All the readings were corrected to the hydrogen gas scale.

Heat Loss in Transfer of Charge to Calorimeter.—In the experiments with the "method of mixtures," the heat loss in the transfer of the metal from the furnace to the calorimeter constitutes a possible source of error which demands careful scrutiny.

On consideration it will be seen that the relative magnitude of this heat loss diminishes with increase in the size of the specimen transferred, and in this investigation the samples varied from 1 to 5 kilograms in weight. In addition, the metal, whether solid or liquid, was always inserted into a crucible, and a "blank" test carried out with the empty crucible. It is reasonable to suppose that approximately the same heat loss would occur when the empty crucible was transferred as when it contained metal, for the actual magnitude of the temperature drop in any case is small and determined solely by the cooling area. The absolute magnitude of this heat loss is difficult to determine accurately, but an estimate of its upper limit was formed by making an experiment with an empty crucible to the surface of which a thermoelement was attached. This crucible was allowed to attain a steady temperature of 500°C., and, with the couple in position, it was transferred from the furnace as far as the calorimeter. The temperature change was observed by the movement of the spot of light of the galvanometer in the circuit of the thermoelectric potentiometer.

The cooling effect in the process of transfer amounted to 2·2°C. As the thermal capacity of the crucible was only about 1/10 of that of the average specimen plus crucible, the cooling of the specimen and crucible would be estimated as 0·2°C. The actual error in the final result is much less than this owing to the compensation provided by using the same procedure for the empty and filled crucible, and we may estimate that it is less than one part in a thousand in the latent heat.

Other Possible Sources of Error.—Besides the sources of error incidental to calorimetric measurements at ordinary temperatures, there was the possibility of heat loss consequent on the use of the inner vessel mentioned above. To avoid the formation of steam when the hot metal strikes the water, the crucible was first transferred into a vessel suspended below the opening of the calorimeter, the opening of the calorimeter being closed promptly after the insertion of the charge, and the vessel was then submerged some time later, so the possible heat loss from the lid needs consideration.

In the first place, it should be noted that the vessel was deep enough for the greater portion of the radiation from the crucible to be absorbed by the water surrounding the vessel. Of the heat which is radiated directly to the lid, most is absorbed by the thick copper and conducted to the water, but a small fraction of it is radiated from the exposed surface of the lid to the surroundings. This "radiation loss" from the lid was studied in some preliminary experiments in which the actual temperatures of the lid, the top and the sides of the calorimeter were observed by the aid of thermoelements pegged into the metal at various points. Hot metal was poured directly into the container and the temperatures of the calorimeter surface at various points observed for a considerable interval of time afterwards.

The maximum difference of temperature between the lid and the body of the calorimeter occurred after the lapse of 5½ minutes from the instant of pouring in the metal, by which time the metal had solidified and cooled very considerably. Now the average heat loss during this interval can be computed as that from a plate which is at an excess temperature of 0·7°C. above its surroundings during a time interval of 5½ minutes. This radiation from the plate was calculated to be 1·3 calories while the convection would be about six times this amount, or 7·8 calories.

Hence the total heat loss from the lid would amount to some 9 calories. This quantity may be compared with a minimum of 30,000 calories conveyed to the calorimeter by the hot metal.

That the use of the inner vessel leads to no errors of measurable amount has also been proved in two other ways. In the one a crucible of molten metal was allowed to remain in it for 22 minutes before submerging in the water. The total heat calculated from this experiment was found to be 3 per cent. low as compared with the values obtained in normal experiments. If the magnitude of the error is assumed to be roughly proportional to the time, then, had the normal procedure been followed, the container would have been submerged within 3 or 4 minutes, and the error would, therefore, be of the order of 0·2 per cent. It must be remembered, however, that the error caused by the "radiation" loss from the lid during the initial stage is even smaller than this, as the excess temperature is not produced immediately.

It might be noted in passing that experiments have been carried out similar in all respects except that in the one case the container has been used, while in the other, it has been dispensed with and the charge dropped into the water. There is, of course, always the possibility of steam formation in the latter case, but the quantity formed is variable. Usually the difference in the results obtained did not exceed ½ per cent.

The remaining sources of error in the calorimetric measurements may be discussed very briefly. The smallest temperature rise was 0·8°C., and was measured to 0·001°C. There was no correction for cooling of the calorimeter during the experiment. The largest rises were about 12°C., and the corrections were applied for heat loss from the calorimeter by the usual method, measuring the rate of fall of temperature after the maximum rise was attained. The temperature rises were corrected for calibration errors of the thermometers, and for the emergent stem error.

The mass of water used was weighed each time in the earlier experiments. Later, a measuring vessel holding about 10,000 cubic cm. was used as a measure, the weight to fill it to a definite mark on the narrow neck being found by weighing. The water equivalent of the calorimeter with its fittings was estimated by weighing it, and calculating from the specific heat. The same procedure was used for obtaining the water equivalent of the inner vessel and of the thermometer. The water equivalent of the calorimeter is probably known to the same order of accuracy as the quantity of water used in the calorimeter.

Results.—Each experiment gives the total heat over a temperature range from that of the furnace down to that of the calorimeter. Now the temperature of the calorimeter varies, being dependent on the temperature rise obtained, so to refer to a common datum temperature it has been necessary to apply a small correction to the results to reduce them to total heats from a specified temperature. This correction was calculated from the known approximate value of the mean specific heat at room temperatures. The total heat values were then plotted against temperature, and a smooth curve drawn through the experimental points. These curves are shown in Figs. 2 and 3 for the metals studied. It will be noted that in the cases of antimony and aluminium, there are experimental points below the observed freeze point, which clearly fall on the curve for the liquid state. Evidently these are due to under cooling of the liquid. The actual freezing point was determined for each metal used by taking a cooling curve with the same thermocouple. Then

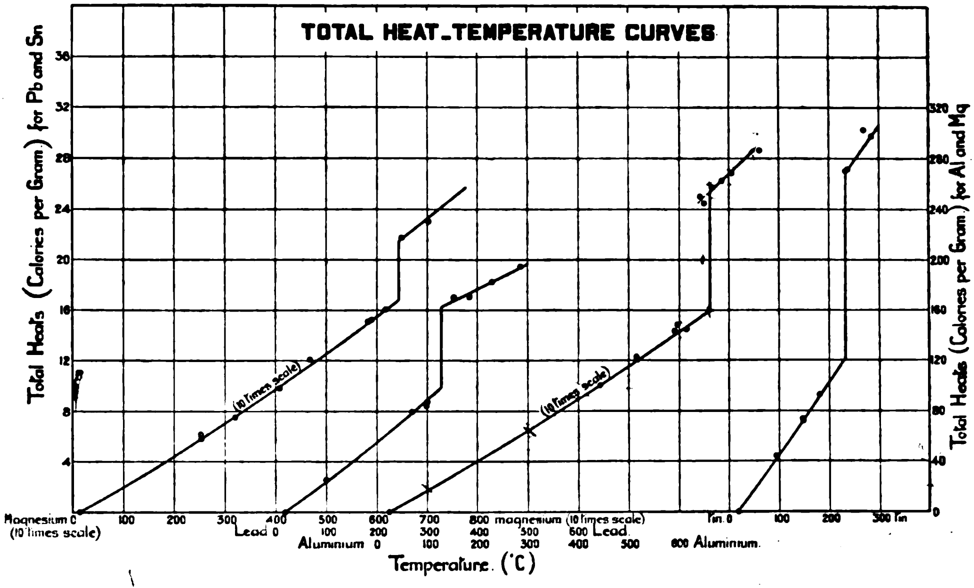


FIG. 2.

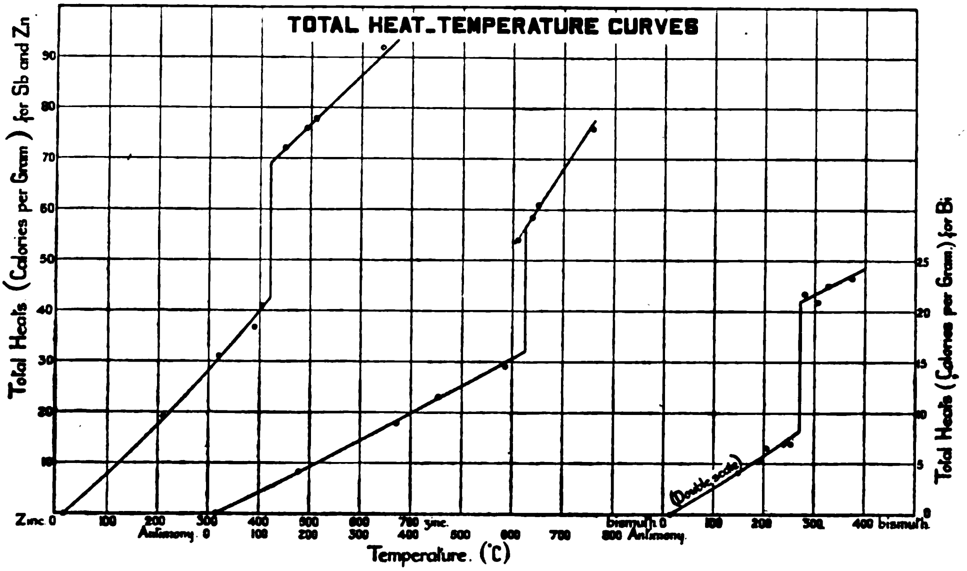


FIG. 3.

the latent heat is the difference between the total heats of solid and liquid, the specific heat being given by the slope of the curve.

A typical experiment on aluminium will serve as an example for all the metals :—

Initial temperature of water in calorimeter	19·08°C.
Final temperature (corrected for radiation losses)	23·80 „
Rise	4·72°C.
Correction for emergent stem	0·01 „
Calibration correction	−0·08 „
Corrected rise	4·65°C
Heat capacity of water (from its mass)	28,858 gms.
Heat capacity of calorimeter	1,821 „
Heat capacity of accessories	28 „
Total heat capacity	30,707 gms.
.·. Heat given up by metal and crucible	142,800 calories
Heat given up by crucible (from separate series of experiments)	28,255 „
Heat given up by metal	114,545 calories

Weight of metal=782 gms.

.·. Heat given up per gm. of aluminium in cooling from 615°C. to 24°C. ... ... =146·5 calories

Approximate specific heat of aluminium ... ... = 0·22 „

.·. Heat from 24°C. to 20°C.=0·9.

Corrected total heat (to 20°C.) ... ... =147·4 „

The remainder of the results for aluminium are given in Table below and Fig. 2.

Aluminium.—The material employed was the purest supplied commercially, the chief impurities being iron (0·13 per cent.) and silicon (0·15 per cent.). The melting point was found to be 656·5°C.

Heat given up by Aluminium in Cooling from θ to 20°C.

θ	Total Heat.	θ	Total Heat.	θ	Total Heat.
20	0·0	591	143·9	650	244·7
443	100·1	597	147·9	664	257·4
516	120·2	615	147·4	686	262·0
516	122·1	640	250·0	706	268·6
				763	286·7

Total heat at melting point—Liquid ... ... 252·6
Solid ... ... 160·2

Latent Heat ... ... 92·4 calories per gm.

Mean specific heat liquid from 657 to 760°C.=0·66.

Specific Heat, Solid Aluminium, Deduced from Curve in Fig. 2.

Temperature Range.	Mean Specific Heat.
50° to 150°	$0{\cdot}22_6$
150° to 250°	$0{\cdot}23_4$
250° to 350°	$0{\cdot}24_5$
350° to 450°	$0{\cdot}25_7$
450° to 550°	$0{\cdot}26_8$
550° to 650°	$0{\cdot}28_7$

Comparison with Other Observers.

The total heat has been given by Lascento,(15) Tilden,(18) Schmitz,(19) Voigt,(20 Schubel,(21) Glaser,(13) Magnus,(22) Behn,(23) and Schimff.(24) A study of the observations shows that the low value for the latent heat obtained by Lascento is due to the abnormally high values obtained by him for the total heat of the solid metal. This may have been due to impurities, which would cause the melting point to spread out over a finite range of temperature, with a partial development of " latent heat " at temperatures below the true melting point.

The values given by the various observers for the latent heat are as follows :—

Plonchon	80
Lascento	64
Glaser	77
Wüst	94
Roos	82
	80

The last observer gives two results, one based on his determination of the cooling curve, and one in which he measured the total heat of the liquid. For the reduction of both results he relied on the values in the literature ; in the one case for the latent heats of comparison metals, and in the other for the total heat of the solid material. Wüst's value is extrapolated from a series of experiments on alloys of varying composition.

In addition to these total heats, the true specific heat has been measured, either over a small temperature range or by the electrical method, by the following observers :—

Jaeger and Diesselhorst(25)	18	0·2144
	100	0·2227
Griffiths and Griffiths(26)	−73	0·1899
	−23	0·2045
	27	0·2144
	67	0·2207
	107	0·2263
Nernst and Lindemann(27)	−38	0·1963
	58	0·2098
	160	0·2250
	283	0·2391

It should be stated again that we do not claim that the specific heats deduced by differentiating the total heat curve will compare in accuracy with direct " electrical method " determinations. Nevertheless, the agreement between our values and the others is as good as the agreement of the others among themselves.

Antimony.—This was kindly supplied to us by Mr. Cookson, of the firm of

Cookson & Co., through the good offices of Dr. Hutton, Director of the Non-ferrous Alloys Research Association. Its purity was stated to be 99·95 per cent., and the melting point as determined by us was 630°C.

The experimental results are given in the table below :—

Total Heat, Antimony.

Temperature.	Total Heat.	Temperature.	Total Heat.
17	0·00	609	54·11
176	8·30	638	58·59
372	18·06	650	61·00
453	23·14	755	75·98
592	29·06		

From the smooth curve :—

Total heat at melting point—Liquid	... ...	56·52
Solid	... ...	32·21
Latent Heat	... ...	24·3

Mean specific heat liquid from 630 to 760°C.$=0·15_5$.

Specific Heat, Solid Antimony.

Temperature Range.	Mean Specific Heat.
150° to 250°	$0·052_4$
250° to 350°	$0·053_1$
350° to 450°	$0·053_7$
450° to 550°	$0·054_4$
550° to 620°	$0·054_9$

Comparison with Other Observers.

Values for the total heat have been obtained by Schubel,(21) Behn,(23) Ewald,(28 Schimff(24) and Gaede.(29) The only observer we can trace who has given a value for the latent heat is Wüst,(14) his value being 38·9. No determinations of the specific heat appear to have been made, apart from those cited above as determinations of the total heat.

Bismuth.—The samples employed were also obtained for us through Dr. R. S. Hutton, from Messrs. Johnson, Matthey & Co., and the chief impurity was silver, to the extent of 0·013 per cent. We found that the freezing point was at 269°C.

The observations were as follows :—

Total Heat, Bismuth.

Temperature.	Total Heat.	Temperature.	Total Heat.
15	0·00	254	6·89
150	4·11	279	21·75
195	5·41	306	20·82
206	6·58	327	22·49
240	6·96	376	23·33

The values for the total heat of the liquid are rather unsatisfactory, possibly owing to some oxidation, and the accuracy of the latent heat will consequently be lower.

The results deduced are given below :—

Total heat at melting point—Liquid...	21·3
Solid	8·3
Latent Heat	13·0

Mean specific heat liquid from 270 to 400°C.=0·019.

Specific Heat, Solid Bismuth.

Range.	Specific Heat.
50° to 150°	$0{\cdot}029_2$
150° to 250°	$0{\cdot}034_9$

Comparison with Other Observers.

Experiments on the total heats have been described by Voigt,⁽²⁰⁾ Schubel,⁽²¹⁾ Stucker,⁽³⁰⁾ Ewald,⁽²⁸⁾ Magnus,⁽²²⁾ Person⁽²⁾ and Schimff.⁽²⁴⁾

The latent heats given by others are quoted below :—

Observer.	Latent Heat.
Person	12·6
Mazzotto	12·4
Iitaka	12·2
Wüst	10·2

The same remarks apply to the results of Wüst for bismuth as in the case of aluminium.

Lead.—The analysis of this showed the presence of 0·002 per cent. iron and 0·002 per cent. copper. It dissolved a little iron from the crucible, and after the experiments was found to contain 0·012 per cent. of iron. The oxygen was also determined afterwards and found to be 0·0046 per cent. by weight. The freezing point of the lead used was 326·5°C.

The following table gives the observations :—

Total Heat Load.

Temperature.	Total Heat.
18	0·00
100	2·52
269	7·94
288	8·41
300	8·72
354	17·04
385	17·05
429	18·29
486	19·42

Total heat at melting point—Liquid	16·18
Solid	9·92
Latent Heat	6·26

Mean specific heat liquid from 330 to 500°C.=$0{\cdot}020_5$.

Specific Heat, Solid Lead.

Temperature Range.	Specific Heat.
100° to 200°	$0{\cdot}031_1$
200° to 300°	$0{\cdot}034_0$

Other observers have given the following values for the latent heat :—

Mazzotto(10)	5·37
Spring(3)	5·32
Robertson(7)	6·45
Glaser(13)	4·78
Iitaka(17)	5·52
Wüst(14)	5·47
Person(2)	5·37
Roos(12)	6·37

Magnesium.—This metal oxidises extremely at temperatures just above its melting point. In addition, it reacts to a measurable extent with water at considerably lower temperatures. After a number of trials, it was found that the only way to prevent errors due to these causes was to enclose the sample completely in a metal container with all joints welded. The magnesium was cast into a block, turned down in a lathe to remove any oxide on the surface, and placed in the crucible (Fig. 4). The lid was then welded on. Thus no air beyond the amount initially present could enter, and the water of the calorimeter was also denied access to the magnesium. The shape of the crucible was intended to give it strength for resisting atmospheric pressure when only fluid was inside, without having to make it so

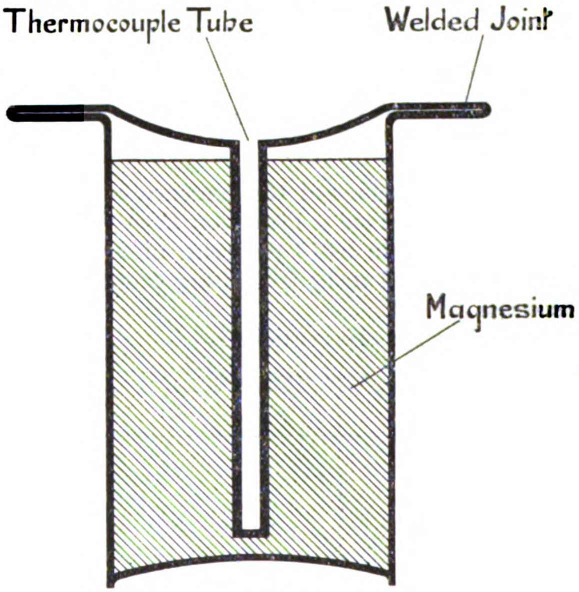


FIG. 4.

thick that its heat capacity would be a serious fraction of the total. The flange at the top serves to this end, and also removed the danger of setting fire to the magnesium when the lid was being welded on. It will be noted that the re-entrant tube for the thermocouple is attached to the lid in such a way that strains on solidification will not break it off.

One effect of completely sealing the sample inside a crucible was to increase the time taken for the calorimeter temperature to become steady on immersing the crucible. The final temperature was not attained, in fact, for about 10 or 15 minutes. Thus the heat loss from the calorimeter during the heat exchange required a somewhat larger correction than was the case in experiments with other metals; for example, in one experiment the observed rise was 4·92°C., and the correction deduced from the rates of cooling before and after, was 0·053°C., a correction of fully 1 per cent.

The analysis of the sample of magnesium gave silicon 0·05 per cent., iron 0·02 per cent. The melting point being at 644°C.

The results are very concordant and are summarised below :—

Total Heat, Magnesium.

Temperature.	Total Heat.	Temperature.	Total Heat.
16	0·00	582	151·6
252	58·2	589	152·4
252	61·6	618	160·6
319	75·8	649	217·4
407	98·0	703	230·2
466	120·2	750	254·0

Total heat at melting point—Liquid	215·9
Solid	169·4
Latent Heat	46·5

Mean specific heat of liquid from 650 to 750°C.$=0{\cdot}26_6$.

Specific Heat, Solid Magnesium.

Temperature Range.	Specific Heat.
150° to 250°	$0{\cdot}025_8$
250° to 350°	$0{\cdot}026_4$
350° to 450°	$0{\cdot}028_0$
450° to 550°	$0{\cdot}029_6$
550° to 625°	$0{\cdot}030_0$

Roos found the latent heat to be 72.

Tin.—The tin employed melted at 232°C. and had the composition :—

Carbon	0·02 per cent.
Lead	Trace
Iron	Trace
Tin (by difference)	99·98

The individual determinations of the total heat gave the results below :—

Total Heat, Tin.

Temperature.	Total Heat.
18	0·00
93	4·45
148	7·22
148	7·37
180	9·25
233	27·01
237	27·19
270	30·24
287	29·76

Total heat at melting point—Liquid	26·90
Solid	12·27
Latent Heat	14·6

Mean specific heat liquid from 230 to 300 °C.=0·056.

Specific Heat, Solid Tin.

Temperature Range.	Specific Heat.
50° to 150°	$0{\cdot}056_9$
150° to 250°	$0{\cdot}058_1$

Comparison with Other Observers.

Iitaka and Pionchon have both quoted values for the specific heat of the liquid, and the latent heats given by a number of observers are collected in the table below.

Observer.	Latent Heat.
Rudberg	13·3
Person	14·3
Pionchon	14·6
Spring	14·65
Mazzotto	13·6
Robertson...	14·05
Glaser	13·6
Roos	14·2
Iitaka	13·4
Wüst	13·8
Guinchant...	14·3

Zinc.—This was a very pure electrolytic zinc, freezing at 420°C. The results were :—

Total Heat, Zinc.

Temperature.	Total Heat.
18	0·00
210	19·20
321	31·13
391	36·62
404	40·91
449	72·04
491	75·83
510	77·89
641	91·51

Total heat at melting point—Liquid	69·23
Solid	42·65
Latent Heat	26·6

Mean specific heat liquid from 420 to 500°C.=0·092.

Specific Heat, Solid Zinc.

Temperature Range.	Specific Heat.
100° to 200°	0·099
200° to 300°	0·105
300° to 400°	0·118

These increase more rapidly than usual with increase of temperature, indicating that the total heat curve should probably run somewhat higher at the intermediate temperatures. However, the difference in the total heats, to bring the specific heat curve down to a straight line is quite insensible in its effect on the total heat at any particular temperature.

Previous results for the latent heat have varied from 23 to 30, as shown in the table below:—

Observer.	Latent Heat.
Mazzotto	28·0
Person	28·1
Heycock and Neville	28·3
Lascento	27
Greenwood	26
Wüst	23
Glaser	29·9
Iitaka	23·1

The only value we have found for the specific heat of the liquid is that of Iitaka, 0·121.

ACKNOWLEDGMENTS.

The investigation arose out of an inquiry of the Non-Ferrous Metals Research Association for information as to the thermal constants of the commoner metals. The authors desire to record their indebtedness to Dr. R. S. Hutton, Director of the Association, for his co-operation in securing suitable pure material; to Dr. Kaye, Superintendent of the Physics Department, for the facilities for carrying out the work; to Mr. A. R. Challoner, Observer, for his assistance in the construction of the apparatus and in helping with the observational work. We are also indebted to Miss V. M. Gayler, D.Sc., for several of the references.

REFERENCES.

(1) Rudberg. Pogg. Ann., 19, 133, 1830.
(2) Person. (*a*) Ann. Chem. Phys. (3), 24, 136 and 274, 1848.
(*b*) Pogg. Ann., 76, 432, 1849.
(3) Spring. Bull. Bruxelles, 11, 400, 1886.
(4) Pionchon. (*a*) C.R., 103, 1122, 1886.
(*b*) C.R., 11, 106, 1887.

(5) Richards. Chem. News. 68, 1893.
(6) Heycock and Neville. J. Chem. Soc., 71, 383, 1897.
(7) Robertson. Proc. Chem. Soc., 18, 131, 1903.
(8) Harker and Greenwood. Engineering, 92, 419, 1911.
(9) Guinchanf. C.R., 145, 320, 1907.
(10) Mazzotto. Atti. Torino., 17, 111, 1882.
(11) Mazzotto. Mem. Inst. Lomb., 16, 1, 1891.
(12) Roos. Zs. Anorg. Chem., 94, 329, 1916.
(13) Glaser. Metallurgie, 1, 103, 121, 1904.
(14) Wüst. (*a*) Forsch. Verh. Deutsch. Ing., No. 204, 1918.
(*b*) Forsch. Verh. Deutsch. Ing., No. 241, 1922.
(Abstract in Zs. Instr., 39, 284, 1918.)
(15) Laschtschenko. (*a*) J. Russ. Chem. Soc., 45, 552, 1913.
(*b*) J. Russ. Chem. Soc., 46, 311, 1914.
(16) White. Chem. and Met. Eng., 25, 17, 1921.
(17) Iitaka. Tohoku Univ. Sci. Reports, 8, 99, 1919.
(18) Tilden. Proc. R.S., 71, 220, 1903.
(19) Schmitz. Proc. R.S., 72, 177, 1903.
(20) Voigt. Wied. Ann., 49, 709, 1893.
(21) Schubel. Zs. Anorg. Chem., 87, 81, 1914.
(22) Magnus. Ann. Phys., 31, 606, 1910.
(23) Behn. Ann. Phys., 1, 257, 1900.
(24) Schimff. Zs. Phys. Chem., 71, 257, 1910.
(25) Jaeger and Diesselhorst. Wiss. Abh. P.T. Reichs, 3, 269, 1900.
(26) Griffiths and Griffiths. (*a*) Phil. Trans., 213, 119, 1913.
(*b*) Proc. R.S., 90, 557, 1914.
(27) Nernst. (*a*) Sitz. Akad. Berlin, 261, 1910.
(*b*) Ann. Phys., 36, 395, 1911.
(28) Ewald. Ann. Phys., 44, 1213, 1914.
(29) Gaede. Phys. Zs., 4, 105, 1902.
(30) Stucker. Sitzber. Wien., Akad., 114, 657, 1904.

XXXVIII.—THE PIEZO-ELECTRIC QUARTZ RESONATOR AND ITS EQUIVALENT ELECTRICAL CIRCUIT.

By D. W. Dye, *B.Sc.*
(Of the National Physical Laboratory.)

Received May 4, 1926.

Abstract.

The quartz piezo-electric resonator is examined experimentally and theoretically with special regard to an equivalent electrical system which can represent it.

It is shown that, as theoretically predicted by Butterworth, such a resonator can be represented by an inductance, a resistance and a capacity all in series. These are pictured as in parallel with another small condenser and the whole is in series with a third condenser, the additional condensers representing air-gaps. The equations for the current in an oscillatory circuit, to which the resonator is attached, are developed and it is found that almost perfect agreement exists between the forms of current curve obtained theoretically and experimentally. This agreement is found to hold for longitudinal resonators of as low a frequency as 44,000 and for transverse resonators of as high a frequency as 15,000,000 periods per second.

It is next shown how the logarithmic decrement of the resonator may be obtained from a rectified line plotted from observation on the current in the oscillatory circuit as a function of frequency width across the crevasse which pierces the summit of the resonance curve.

The methods of analysis of the equivalent mesh into its components are next developed and it is shown that this analysis can be effected by carrying out a series of observations of the current at resonance when the air-gaps are varied by known amounts, or when the effective resistance of the oscillatory electrical circuit is given different known values.

The theoretical and experimental results are found to be consistent. The value of the shunting condenser is somewhat smaller than that measured at a neighbouring frequency outside the region of resonance. A possible explanation is offered.

The effects on frequency of response of variation of air-gap are studied and the difference between prediction and observation is discussed. This difference is only a few parts in a hundred thousand. In the case of transverse resonators remarkable effects occur when the air-gap is varied through the regions where its length is an integral member of half-wavelengths of the supersonic air waves produced by the vibration of the quartz.

The temperature coefficient of frequency of a considerable variety of resonators is examined over a range of temperatures up to 40°C. It is found that very diverse results are obtained and probable explanations are offered.

The effects of displacement of the resonator from the position of centrality are examined. These are shown to be small, but not quite negligible.

The current taken by the quartz mesh is then examined in some detail theoretically, and one or two experimental curves are given, together with a graphical method of deducing the curve of current from the constants of the quartz. A selection of theoretical curves for the conditions under which the experiments of Cady were made have been calculated. The curves are in all respects of the shape and form experimentally found by him.

A number of conclusions and suggestions terminate the Paper.

THE quartz piezo-electric resonator has been introduced by Cady who has published a number of valuable Papers(1) on their properties and form. G. W. Pierce(2) also has contributed valuable information on the subject showing the form, mounting and circuits of quartz oscillators whereby the resonant vibration is self-maintained by a valve in the same fashion that a tuning fork may be made self-maintaining. More recently he has published an account of some very accurate measurements of the velocity of sound at very high frequencies, using quartz oscillators as the source of sound.

Giebe(3) also has published a short Paper indicating a simple and elegant means whereby the state of maximum resonant vibration may be rendered directly visible by mounting the resonator in a vacuum and observing the luminous glow between the surfaces of the quartz and the electrodes, consequent upon the large voltage gradient in the air gap at the regions where the alternating stress in the quartz is a maximum. In this manner the overtone modes of vibration may be rendered visible also. Other more or less popular accounts of the properties of quartz resonators and oscillators have from time to time appeared in the technical press.

The reader is specially referred also to the classical Paper by Sir W. Bragg(4) on the structure of α and β quartz.

Although, therefore, the form, construction and use of quartz resonators and oscillators may be considered fairly well known it is, perhaps, desirable to include in the present Paper the briefest description of the essentials of a piezo-electric quartz resonator.

. Referring then to Fig. 1, we have a transverse section of a natural quartz crystal cut in a plane perpendicular to the optic axis. Any such section contains three electric axes (shown dotted), at angles of 120° to each other and parallel to the rectangular bounding faces of the crystal.

A bar or plate is cut from the section with its length perpendicular to one of the electric axes as shown at *AB*. The dimension of the piece in the direction parallel to the optical axis of the crystal may be large or small. If it is small compared with the length *AB* we obtain a bar. If of the same order as *AB* we obtain a plate. If such a plate or bar is placed in an electric field applied in a direction perpendicular to its length, i.e., parallel to the electric axis, *ab*, the bar will experience two strains, one in the direction of its length and the other perpendicular thereto, i.e., along the direction of the applied field. These two strains are of opposite sign, so that, if for example, the bar becomes longer in the direction *AB* it becomes thinner in the direction *ab*. The two strains are such that the volume remains constant.

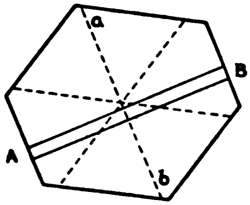


FIG. 1.—CROSS-SECTION OF QUARTZ CRYSTAL SHOWING HOW A BAR OR PLATE IS CUT.

The strain across the bar has been called the longitudinal effect because it is along the direction of the applied field although transverse to the length of the bar.

It is clear that if an alternating electric field is applied to the bar it will be subjected to alternating stresses and strains both along its length and transversely thereto.

If the frequency of the applied field is adjusted to coincide with that of one of the free modes of vibration which can be maintained by such alternating stresses, a large resonant vibration will occur. The amplitude of this vibration and its rate of change with frequency will depend upon the mechanical damping of the quartz and upon its piezo-electric reaction on the applied field.

It is the very small damping coefficient and the permanence of form and constitution of natural quartz that render it specially valuable as a radio frequency standard when suitably cut and mounted.

It must be kept in mind in thinking of the various modes of vibration that a longitudinal vibration results from the transverse piezo-electric effect and vice versa.

Now a theorem has been enunciated by Butterworth(5) relating to a dynamical system in which mechanical vibrations may be produced by the reaction of an electric system upon it. It is shown that the mechanical vibrator may be replaced by an equivalent electrical oscillatory circuit coupled to the actual electric circuit in a manner depending upon the nature of the mechanical oscillator and the means whereby the transformation of electric into mechanical displacement occurs. The piezo-electric resonator is a mechanical vibrator falling within this class. For such a resonator the equivalent circuit given by Butterworth—with the addition of a small capacity K_2—is as shown in Fig. 2.

The system consists of an inductance N,* a resistance S and a capacity K all in series. These are shunted by another condenser K_1. Such a mesh represents a piezo-electric resonator in which the electrodes are in contact with the surface of the quartz.

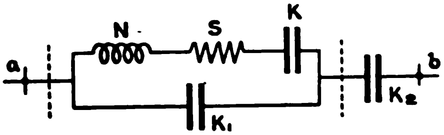


FIG. 2.—THE EQUIVALENT NETWORK REPRESENTING A RESONATOR MOUNTED BETWEEN ELECTRODES.

The constants N, K and S are related to the dynamical properties of the bar as follows—quoting from Butterworth :—

$$N=a/B^2\,;\quad K=B^2/\gamma\,;\quad S=\beta^2/B^2$$

where a, β and γ are the constants of inertia, damping, and restoration respectively in the fundamental equation of motion.

$$(aD^2+\beta D+\gamma)y=Y$$

in which y is the displacement and Y is the displacing force. D is the operator d/dt. The displacing force Y is equal to $B\,e$, where e is the E.M.F. between the two surfaces of the quartz.

The constants a, β, γ are, therefore, simple physical constants of the quartz, whilst B is an electro-physical constant proportional to the piezo-electric effect. The value of B is measured by the mechanical stress produced per unit of electric field applied. It is analogous to the constant which would define the back E.M.F. produced in a wire vibrating in a magnetic field.

In the case of a bar or plate vibrating under its own internal stresses the constants of inertia, restoring force and damping are, of course, distributed. For any given mode of vibration there will, however, be equivalent concentrated inertia, damping and restoring forces which may be considered constant for that mode.

---

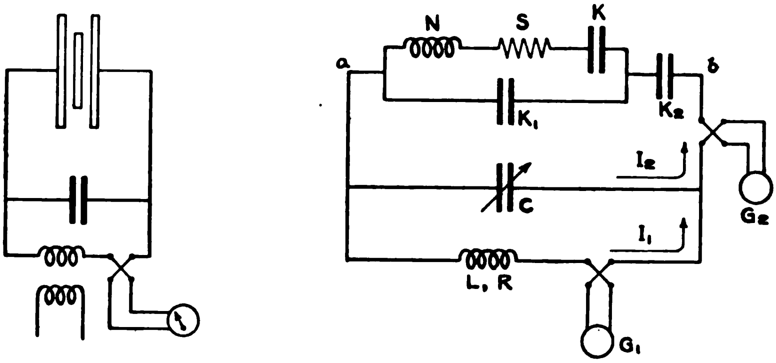
* Since writing this Paper a note has appeared in the Physical Review (Vol. 25, No. 6, Abs. 52, p. 895, 1925) which gives identically the same circuit for the quartz resonator, but the theorem referred to was published, and the experiments described here were in progress before this note appeared.

If the resonator vibrates in an overtone mode such as that representing 3, 4, 5, 6, etc., segments, there will be a corresponding set of equivalent constants N, S and K, which will apply only to that mode.

It is not proposed in the present Paper, to examine closely the mathematical nature of the general equations given above in relation to the possible modes of vibration of the system, but to examine rather both algebraically and experimentally some of the properties of the equivalent electrical system of Fig. 2, and of other circuits upon which the resonance of a quartz resonator may be observed.

The resonator as usually mounted consists of a plate or bar of quartz in which the electrodes are separated from the surfaces of the bar by a small air gap. In this case we may represent the air gap by a small condenser K_2 in series, as shown in Fig. 2.

A very satisfactory method of using a resonator as a standard is that given by Cady in which the resonator with its electrodes is connected in parallel with the condenser of an oscillatory circuit tuned approximately to the resonance frequency of the quartz. A current-measuring device in series with the inductance coil of the oscillatory circuit indicates the sudden change in current occurring at the response frequency of the quartz.



(a) (b)

FIG. 3.—MODE OF OBSERVING RESONANCE ON A RESONATOR AND THE EQUIVALENT ELECTRICAL SYSTEM.

This arrangement is shown diagrammatically in Fig. 3(*a*) and the complete electrical equivalent system is as shown in Fig. 3(*b*).

In this figure the piece of quartz itself is represented by N, K and S shunted by K_1. The two air gaps are represented by K_2.

A series of careful experiments is able to determine the validity or otherwise of the equivalent electrical network and will give valuable information regarding the actual values of the equivalent constants N, S and K and show how these depend upon the properties of the quartz, etc.

It is to be anticipated also that much may be learned regarding the constancy of these quantities with respect to the physical condition of the specimen and its surroundings.

The experiments described herein have shown that a striking agreement may be obtained between the observed current I_1 (Fig. 3*b*) in the oscillatory circuit as a function of the frequency of the source and the calculated current in terms of the determined constants N, S, K and K_1. Equally good agreement is also obtained between theory and experiment with respect to the current I_2 (Fig. 3*b*) in the shunt circuit containing the resonator.

Before giving the experimental results and the comparison with those calculated it will be found helpful, in the formation of a clear mental image of the behaviour of the resonator, to consider the properties of the equivalent electrical mesh representing the resonator itself as an entity apart from the attached electrical circuit. We will then proceed to an examination of the properties of the complete system and will show how the analysis of the constants N, S, K and K_1 may be obtained from the experimental observations.

Referring to the mesh N, S, K, K_1 of Fig 3(*b*) we can find an equivalent virtual single series circuit consisting of an effective pure resistance S_0 in series with an effective pure capacity K_0 to replace the mesh. The values of S_0 and K_0 will, of course, be greatly dependent upon frequency. The equivalents S_0 and K_0 will be in series with K_2 and it is this simple series circuit which is in parallel with the oscillatory circuit.

It is convenient to use a resonant frequency, $\omega_0/2\pi$ defined by $NK\omega_0^2=1$ and to write q for $1-NK\omega^2$, where q is a small quantity proportional to a small change in frequency from that given by $\omega_0/2\pi$.

This expression constantly occurs in what follows. The frequency $\omega_0/2\pi$ will be spoken of as the true resonant frequency, although such a definition is open to some criticism. Another quantity of great importance is the term $SK\omega$, a quantity equivalent to the power factor of the condenser K.

$SK\omega\times\pi$ is equal to the logarithmic decrement per complete period of the resonator, and will be designated δ_2. To avoid the constant repetition of π in the formulæ $SK\omega$ will be written as φ_2, so that $\delta_2=\varphi_2\pi$.

Using this nomenclature it will be found that the quantities S_0 and K_0 are given by the expressions :—

$$S_0=\frac{SK^2}{K_1^2[\varphi_2^2+(q+K/K_1)^2]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

and

$$\frac{1}{K_0\omega}=\frac{\varphi_2^2+q(q+K/K_1)}{K_1\omega[\varphi_2^2+(q+K/K_1)^2]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

The magnitude which these quantities can assume is dependent mainly upon φ_2. This is a very small quantity—of the order 30×10^{-6} in a good specimen of quartz.

It is a property of a resonant electrical circuit that if for various chosen values of q as defined above we plot corresponding values of S_0 and $1/K_0\omega$ as ordinate and abscissa respectively, we shall obtain an almost perfect circle. From equation (*b*) it will be seen also that K_0 can assume negative values for values of q lying between 0 and $-K/K_1$. This is a very important property of the quartz, and is responsible for its behaviour when placed in an air gap between two electrodes. Since it so happens that K/K_1 is a quantity of the order 1/100, the region of frequency through which $1/K_0\omega$ can be negative is small.

We have seen that the air gaps are considered as equivalent to a small series condenser K_2. If for any particular air gap represented by K_2 we choose such a value of q that $K_0 = -K_2$ the whole system between the points *ab* of Fig. 2 becomes equivalent to a non-inductive resistance S_1. It is clear that the maximum damping is produced upon the oscillatory circuit almost at this frequency. It is necessary to give the frequency at which this effect occurs a different name from the resonant frequency $\omega_0/2\pi$ as previously defined. It can be called the response frequency of the quartz. It differs theoretically from ω_0 by the quantity $-\frac{\omega_0 q_1}{2\pi}$, where q_1 is that value of q at which $K_0 = -K_2$. This condition is shown vectorially in Fig. 4. The curve AB shows a small part of the vector impedance circle diagram resulting from plotting $1/K_0\omega$ as abscissa against S_0 as ordinate for various values of q. Suppose the air gap is such that $1/K_2\omega$ is given by OQ, then, at a certain negative value of q represented by the point P on the curve, the value of $1/K_0\omega$ represented by ON will be equal and opposite to OQ. The resultant vector impedance across "*ab*" of Fig. 3(*b*) is therefore OT. With a larger air gap and hence a smaller value of K_2, the negative reactance $K/K_2\omega$ shown as OQ_1 will be greater. The response frequency will then occur at such a value of q as is represented on the curve AB by the point P_1. This is the larger negative value of q requisite to make ON_1 equal to OQ_1.

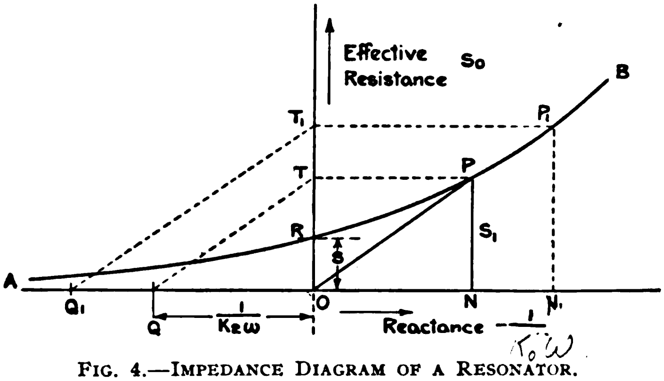


FIG. 4.—IMPEDANCE DIAGRAM OF A RESONATOR.

The effective resistance of the whole resonator has now the greater value OT_1, which will, therefore, not cause such a large reduction in the current in the oscillatory circuit *LRC*.

From these considerations it will be seen that the frequency of response is not quite equal to that which has been defined as the true resonant frequency of the quartz itself, but is a function of the air gap. When K_2 is infinite (no air gap) the response frequency is at the true resonant frequency, where $q=0$ and the vector impedance becomes S as shown by OR in Fig. 4.

It is perhaps desirable at this stage to anticipate the experimental results somewhat by giving the actual effective values of K, S, N and K_1 experimentally measured in a typical resonator.

For a bar about 7 cm. long, 0·15 cm. thick and 0·6 cm. wide, the following values have been found :—

$K=0{\cdot}08\ \mu\mu$ F.
$S=1{,}500$ ohms.
$N=160$ henries.
$K_1=8\ \mu\mu$ F.
$\omega_0=275{,}000$.

It will be seen that the reactance of K and N are very large indeed.

$\varphi_2=SK\omega$ is of the order 30×10^{-6}, giving the extremely small value of 1×10^{-4} for δ_2 the log. dec. of the resonator.

The diameter of the motional impedance circle of Fig. 4 is no less than 100 megohms. In order to show the resistance vectors OR, OT, etc., it has been necessary to magnify the ordinates by about 50, so that the circle really becomes an ellipse with a vertical axis. Since OR represents 1,500 ohms the major axis of the ellipse is about 300 metres long if OR is 5 mm. in the diagram.

We will now return to a consideration of the resonance curve of current in the inductance coil L of the oscillatory circuit LRC across which the resonator is shunted. It is this current which can easily be observed as a function of frequency, and of those other quantities in Fig. 3(*b*) which can be varied. By deductions made from the observations we can arrive at a complete analysis of the constants K, S, N and K_1.

The case under investigation is as shown in Fig. 5.

The resonator is the mesh $NSKK_1$, with air gaps between the surfaces of the quartz and the electrodes represented by K_2.

This system has flowing through it a current of which the instantaneous value is represented by i_2. It is shunted across the oscillatory circuit CLR, carrying the current having an instantaneous value i_1. An electromotive force e_0 (assumed constant) is induced in L by very loose coupling to a source of smoothly variable frequency as indicated. A fictitious current i_3 flows in the quartz mesh itself. This cannot be measured, but is introduced for purposes of the algebra of the analysis. It has its counterpart in the physical reaction of the quartz.

The root mean square value of i_1 is measured by heater and thermo-junction connected to galvanometer G_1. Similarly I_2 is measured on G_2. This measurement is difficult owing to the smallness of I_2 and to the smallness of the energy circulating in the shunt system.

When the frequency of the source is smoothly varied through the region of response of the quartz, remarkable changes occur in the values of I_1 and I_2. Owing to the relatively large and sudden absorption of energy by the quartz at the frequency of response the current I_1 falls very rapidly to a very sharply defined minimum, and then rapidly rises again to nearly its previous value. The resonance curve of I_1, which, in the absence of the quartz, assumes a normal shape, has thus a deep and narrow crevasse. This is, of course, well known as a result of the work of Cady and others, and examples are given in his excellent Paper on the subject. The current I_2 rises to a sharp maximum, and suddenly falls to a small value again. The exact form of the curve I_2 and its location with respect to I_1 is, however, considerably dependent upon the conditions under which the experiments are carried out, as will be seen later.

The equations connecting the currents and voltages represented in Fig. 5 are

$$(R+La)i_1+\frac{1}{Ca}(i_1-i_2)=e_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{Ca}(i_2-i_1)+\frac{1}{K_2a}i_2+\frac{1}{K_1a}(i_2-i_3)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$(S+Na+1/Ka)i_3+\frac{1}{K_1a}(i_3-i_2)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a is written for $j\omega$.

Both from an experimental and from a theoretical standpoint it is convenient to calculate I_1 in terms of I_0, when I_0 is the current which is obtained in the oscillatory circuit when in resonance in the absence of the quartz. We can then write $\sigma_1^2=I_1^2/I_0^2$, where σ_1 is always less than unity.

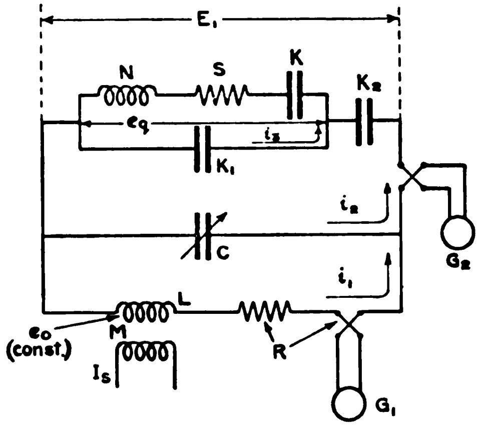


FIG. 5.—CIRCUIT DIAGRAM OF RESONATOR CONNECTED IN PARALLEL WITH AN OSCILLATORY CIRCUIT.

By elimination of i_3 and i_2 in the above equations and by putting $RI_0=E_0$, where E_0 is the r.m.s. value of e_0 in the final equation for I_1, the expression for σ_1^2 will be found to be

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\left(q+\frac{K(C+K_2)}{CK_t+K_1K_2}\right)^2\right]}{\left[pq+p\frac{K(C+K_2)}{CK_t+K_1K_2}-q\frac{K_1K_2}{CK_t+K_1K_2}-\frac{KK_2}{CK_t+K_1K_2}-\varphi_1\varphi_2\right]^2+\left[q\varphi_1+p\varphi_2+\varphi_1\frac{K(C+K_2)}{CK_t+K_1K_2}-\varphi_2\frac{K_1K_2}{CK_t+K_1K_2}\right]^2} \quad . \quad . \quad (4)$$

In order to render the equation more compact the terms

$\varphi_1=RC\omega,$ $\qquad\varphi_2=SK\omega,$
$p=1-LC\omega^2,$ $\qquad q=1-NK\omega^2$ and $K_t=K_1+K_2$

have been substituted for these respective quantities. It will be remembered that $\varphi_1=\delta_1/\pi$ and $\varphi_2=\delta_2/\pi$, where δ_1 is the log. dec. per complete period of the electrical circuit *LRC*, and δ_2 is the log. dec. of the resonator; " q " and " p " are small quantities compared with unity, and to a very close approximation may be considered equal to $\frac{2dn_0}{n_0}$ and $\frac{2dn_1}{n_1}$ respectively, where dn_0 is a small frequency difference from the frequency at which $q=0$ and dn_1 has the same meaning with respect to p.

Now, in the case of quartz, φ_2 is very small indeed—as already anticipated, of the order 30×10^{-6}—and, as a result, σ_1 will assume its minimum value to a very close approximation indeed at that value of q at which the second term in the numerator vanishes—i.e.,

$$q=-\frac{K(C+K_2)}{CK_t+K_1K_2}$$

when σ_1=minimum.

From an experimental standpoint, it is convenient to work in terms of frequency differences, and it is further very desirable to take as datum that frequency at which σ_1 has its minimum value—i.e., the bottom of the crevasse.

The equation can therefore be thrown into this form by substituting a quantity

$$q=-\frac{K(C+K_2)}{CK_t+K_1K_2}-\frac{2dn}{n_0}$$

in place of q.

Equation (4) now becomes, by a further slight simplification,

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{2dn}{n_0}\,\frac{K_1K_2}{CK_t+K_1K_2}-p\frac{2dn}{n_0}-\frac{KCK_2^2}{(CK_t+K_1K_2)^2}-\varphi_1\varphi_2\right]^2+\left[p\varphi_2-\frac{2dn}{n_0}\,\varphi_1-\varphi_2\frac{K_1K_2}{CK_t+K_1K_2}\right]^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation contains no approximations, and will accurately delineate the curve obtained for any condition of the electric circuit. We still have the term p, which changes rapidly with change of frequency when L and C remain constant, and are so adjusted that $LC\omega^2$ is approximately unity.

When testing the validity of the theorem by experiments, the form taken by equation (5) will depend upon the conditions under which these have been carried out.

A number of cases may arise as follows :—

(*a*) Cady's Experiments.—At each adjustment of frequency to a known value the capacity of the oscillatory circuit is adjusted so that, with respect to this adjustment, σ_1 is a maximum.

This case is met by substituting back into (5) the quantity $I-LC\omega^2$ for " p," and then differentiating with respect to C considered as the variable.

Having thus found an expression for the changes in C from some datum value in terms of dn and the other constants, the quantity $C+dc$ must be substituted back into (5) in order to obtain an equation in which " dn " is the only variable.

A very complicated expression results, which entails tedious computations, and does not lend itself well to the derivation of further equations for the values of $\sigma_{1\min}$.

as a function of the rest of the constants of the circuits when these are varied. A fairly good approximation can be made, as shown later, by consideration of p as the only variable.

This method of experimenting is, moreover, extremely laborious to carry out. A small rate of drift of the source will impair the accuracy of the results, owing to the long time taken to observe a complete curve of σ_1.

(b) Another case corresponding somewhat with the above is to adjust the condenser C so that at each frequency $LC\omega^2=1$, i.e., $p=0$.

This case can be carried out fairly easily by disconnection of the resonator from the oscillatory circuit, which is then tuned by adjustment of C to resonance at each frequency adjustment. This setting is best made by a two reading method, since considerable accuracy is necessary.

The observations of σ_1 are now somewhat more quickly made, and in general more accuracy is obtained than by method (a). The equation simplifies to

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{2dnKK_2}{nCK_t}-\frac{KK_2^2}{CK_t^2}-\varphi_1\varphi_2\right]^2+\left[\frac{2dn\varphi_1}{n}+\frac{K_1K_2\varphi_2}{CK_t}\right]^2} \quad . \quad . \quad . \quad . \qquad (6)$$

In this equation CK_t has been used instead of $CK_t+K_1K_2$, since in general the ratio K_1K_2/CK_t is less than 0·005. It will be seen that the equation is simple, and that σ_1 approaches unity rapidly with increasing positive or negative values of "dn."

Another still more convenient method of observation is as follows:—

(c) Having adjusted the frequency so that $\sigma_{1\,\mathrm{min.}}$ is obtained, the resonator is disconnected, and C is adjusted so that $LC\omega^2=1$. The maximum value of σ_1 is adjusted to or called unity.

The complete curve of σ_1 against "dn" is then obtained without further adjustment of C. Under these conditions, "p" is equal to $-\frac{2dn}{n}$ for the small frequency changes in question. Equation (5) then takes the form

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{4dn^2}{n^2}+\frac{2dnK_1K_2}{CK_t}-\frac{KK_2^2}{CK^{\,2}}-\varphi_1\varphi_2\right]^2+\left[\frac{2dn(\varphi_1+\varphi_2)}{n}+\frac{\varphi_2K_1K_2}{CK_t}\right]^2}. \qquad (7)$$

In this equation K_1K_2 has again been neglected in comparison with CK_t.

(d) In the more general case, where C is left unvaried, we may set the oscillatory circuit at any frequency near that corresponding to (a).

It is convenient to call "Δn" the frequency difference between that at which σ_1 is a minimum—i.e., $q=-\frac{K}{K_t}$, and that at which $LC\omega^2=1$, i.e., $p=0$.

We must then substitute in equation (5) $p=-\frac{2dn}{n}-\frac{2\Delta n}{n}$, where Δn is a small frequency difference which does not vary when n is varied.

The equation for this case becomes

$$\sigma_1{}^2 = \frac{\varphi_1{}^2\left[\varphi_2{}^2 + \frac{4dn^2}{n^2}\right]}{\left[\frac{4dn^2}{n^2} + \frac{2dn}{n}\left(\frac{K_1K_2{}^2}{CK_t} + \frac{2\Delta n}{n}\right) - \frac{KK_2{}^2}{CK^2} - \varphi_1\varphi_2\right]^2 + \left[\frac{2dn(\varphi_1+\varphi_2)}{n} + \varphi_2\left(\frac{K_1K_2{}^2}{CK_t} + \frac{2\Delta n}{n}\right)\right]^2} \quad . \quad . \quad . \quad (7a)$$

This equation is useful when it is desired to carry out a series of experiments using various air gaps, as explained later. The frequency of response varies with variation of air gap, as has been shown (Fig. 3). The use of (7*a*) enables us to leave C unchanged notwithstanding the change in response frequency. It is of course necessary to insert the value of Δn appropriate to each observed value of frequency at which $\sigma_{1\text{min.}}$ occurs when the air gap is varied.

In all the equations so far given for σ_1 it will be seen that the crevasse is not symmetrical, since the denominator has values depending upon the sign of "*dn*." For the particular case in which C is so adjusted that $2\Delta n/n = -\frac{K_1K_2}{CK}$ the denominator only contains even powered terms of "*dn*," and hence does not depend upon its sign. For this case, therefore, the crevasse when plotted to a scale of "*dn*" is perfectly symmetrical.

This case is of interest chiefly in connection with determinations of φ_2, since a very simple and accurate expression may be derived from it, as will appear immediately.

In order to be strictly accurate, we should consider φ_1 and φ_2 as variables when "n" is varied, since they contain ω. In practice, however, the range of frequency involved in the interesting part of the curves is so small that, so far as "ω" is concerned, φ_1 and φ_2 may be regarded as constant.

At this stage it is desirable to give some experimental and theoretical examples of curves in order to show the extraordinary accuracy of the agreement which may be obtained and to make clear the effects on the crevasse of varying certain conditions.

In Fig. 6 is an example of a curve of σ_1 for a resonator in the form of a bar approximately 6 cms. ×0·15 cm. ×0·6 cm., vibrating in its fundamental longitudinal mode at a frequency of approximately 44,000 cycles per second.

The case given has been chosen and has been plotted on such a scale as to bring out various points.

The curve has been purposely made unsymmetrical by slightly detuning the electrical circuit, and so corresponds to case (*d*). The electrical circuit is in resonance at a frequency 64 cycles per second lower than the frequency where σ_1 is a minimum.

The flat dotted curve is the curve of current I_0 in the oscillatory circuit that would have been obtained in the absence of the quartz. Owing to the open scale of frequency, the curve loses its more familiar shape, and what usually appear as a sharp peak is now a very rounded top. The whole belt of frequency covered on this curve is 0·5 per cent. wide.

The constants of the circuit and the air gap have been chosen so as to give a very deep crevasse having a minimum value of 0·128.

The curve has not been drawn through the points, but from an equation of the form (7*a*), and the observed points have been very carefully plotted—as dots in circles—afterwards.

It will be seen that the agreement is very striking, and shows that within the accuracy possible experimentally the electrical behaviour of the resonator is exactly represented by the mesh of Fig. 2.

The two parallel dotted lines show a belt of frequency of width of one part in a thousand.

The next sheet of curves, Fig. 7, refers to the same resonator vibrating in the same mode as in Fig. 6. The air gap is slightly larger, the electrical circuit is such that the minimum is not so small as in the previous case, and the curves have been drawn on a very much more open scale of frequency in order to bring out the shape more clearly. The parallel dotted lines show a belt one part in ten thousand wide. In the case of curve A the circuit has been as nearly as possible experimentally tuned to exact resonance at the frequency of maximum response for a case where the quartz crystal is in position but prevented from vibrating.

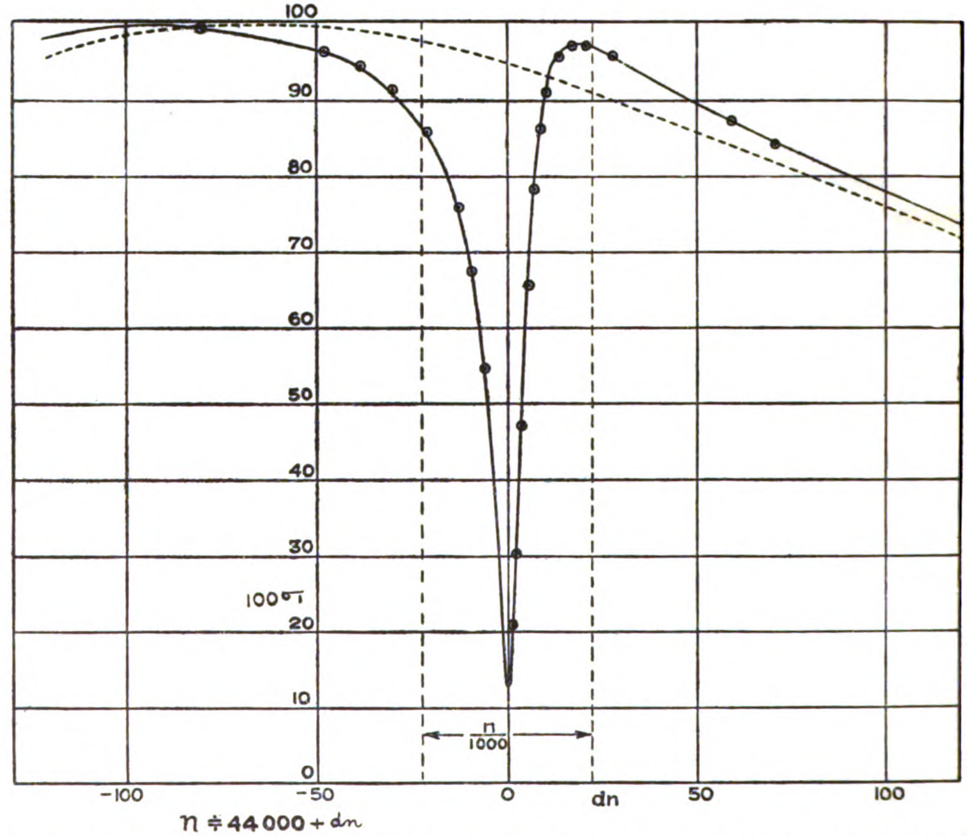


FIG. 6.—RESPONSE CREVASSE IN CURRENT RESONANCE CURVE FOR A LONGITUDINAL RESONATOR.

This corresponds to equation (7*a*), but the quantity $\frac{2\Delta n}{n}$ has been made equal to $-\frac{K_1K_2}{CK_t}$, so that the curve should theoretically be quite symmetrical. Actually this condition is difficult to adjust quite exactly and so a small term equal to $\frac{K_1K_2}{CK_t}+\frac{2\Delta n}{n}$ has been included so as to fit the experimental curve at two suitable points. The departure from symmetry is inappreciable but can be seen by a close inspection. The curve is again that obtained by the equation and the observed points are again shown by the dots in circles. The equation has been chosen to fit three of the points. The accuracy with which it fits the rest of them shows that the equation rightly accounts for the change in the curve consequent upon changing the electrical circuit.

The other curves are all theoretical and have been drawn to bring out the effects of detuning the oscillatory circuit. The curves in order B, C and D represent the currents that will be obtained when the circuit is tuned to frequencies 0·5, 1 and 2·5 per cent. respectively, lower than that of curve A. For these cases the crevasse is on the side of the ordinary resonance curve instead of being on the top as at A.

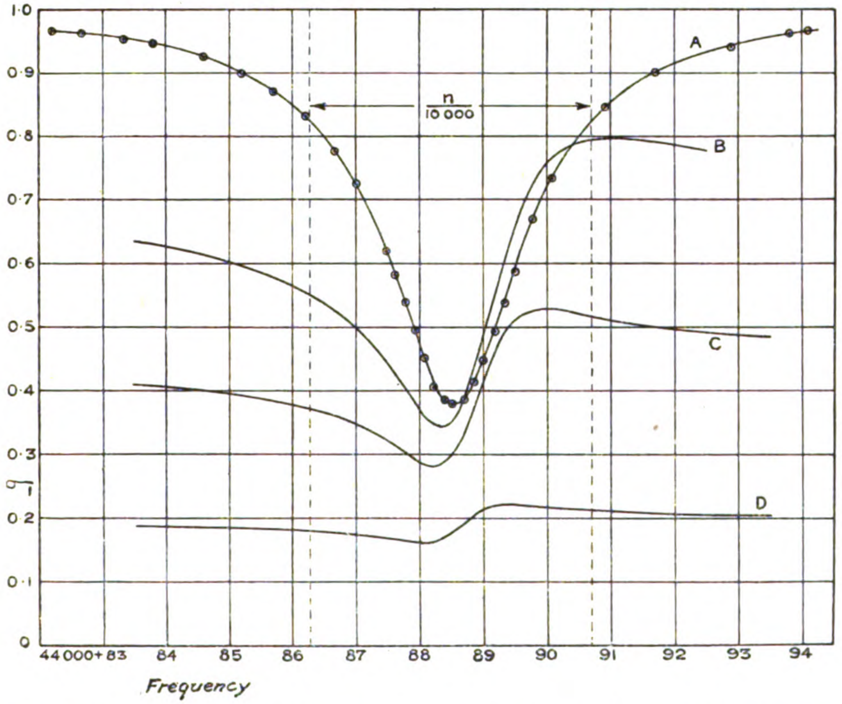


FIG. 7.—RESPONSE CREVASSES SHOWING EFFECT OF DETUNING THE RESONANT CIRCUIT.

It will be seen that the position of $\sigma_{1\text{min.}}$ is slightly altered as a result of the detuning. In the case of curve B, it is about five parts in a million lower than for curve A, whilst for curve D the crevasse is not well defined and occurs very low down on one side of the main resonance curve. The minimum here is displaced by about one part in a hundred thousand from that corresponding to the symmetrical curve.

It is thus seen that the frequency at which $\sigma_{1\text{min.}}$ occurs is almost entirely independent of the precise adjustment of the electrical circuit to resonance. The setting of this circuit can, of course, be made much closer to resonance at the desired frequency than 0·5 per cent. Although it is not always easy to set it to one part in ten thousand it can always be set to one part in one thousand. For an uncertainty of this amount the uncertainty of the response frequency of the resonator will not be so great as three parts in a million.

The next curve (Fig. 8) represents a resonator of much higher frequency and of a different type. In this case the resonator is in the form of a small rectangular slab 1·564 cm. × 1·640 cm. × 0·615 cm. thick. This resonator is one which is suitable for the transverse mode of vibration. This particular piece was chosen with special care and is very homogeneous and has a very small logarithmic decrement. It will oscillate readily when suitably connected up with a valve.

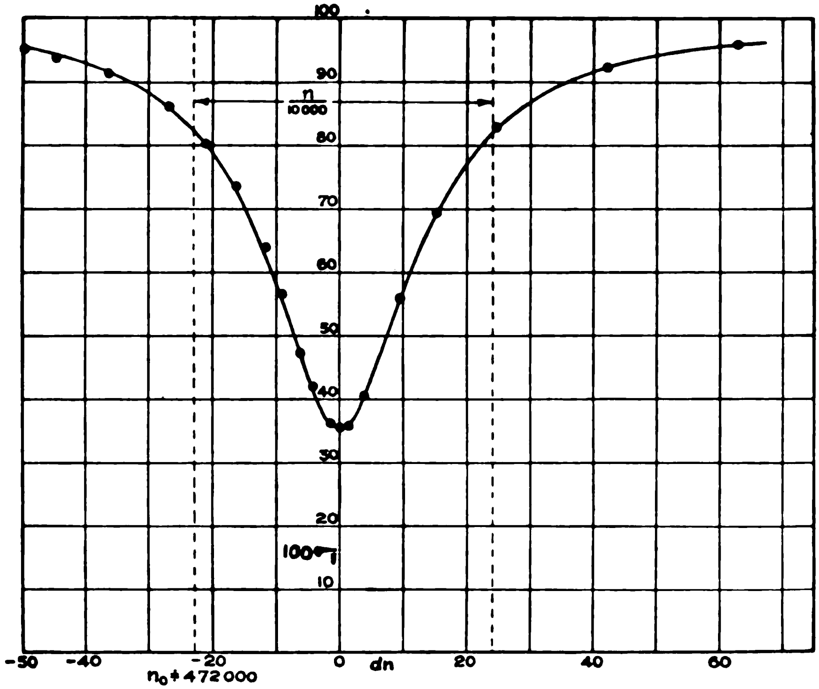


Fig. 8.—Response Crevasse for a Transverse Resonator.

The curve corresponds to a nearly symmetrical case. The resonant frequency is approximately 472,000 and the log. dec. is only $0{\cdot}8 \times 10^{-4}$. The main part of the crevasse is comprised within the belt of 1 in 10,000 embraced by the dotted lines.

The remarkable agreement between the observed points (dots in circles) and the calculated curve shows that for a transverse resorator the theory also holds within the experimental limits. The equivalent electrical constants of a given piece of quartz are, of course, quite different according to whether it is vibrating in a longitudinal or in a transverse mode, but in general the log. decs. are about the same and the value of K_1 is not very different for the two modes of vibration.

As might be expected, the damping coefficient for a short high-frequency resonator is not very different from that for a long low-frequency resonator.

As an extreme case, in Fig. 9 is given a curve for a resonator of no less a frequency than 15×10^6. This resonator is in the form of a small disc about 0·2 mm. thick and 6 mm. diameter. Its mode of vibration is transverse.

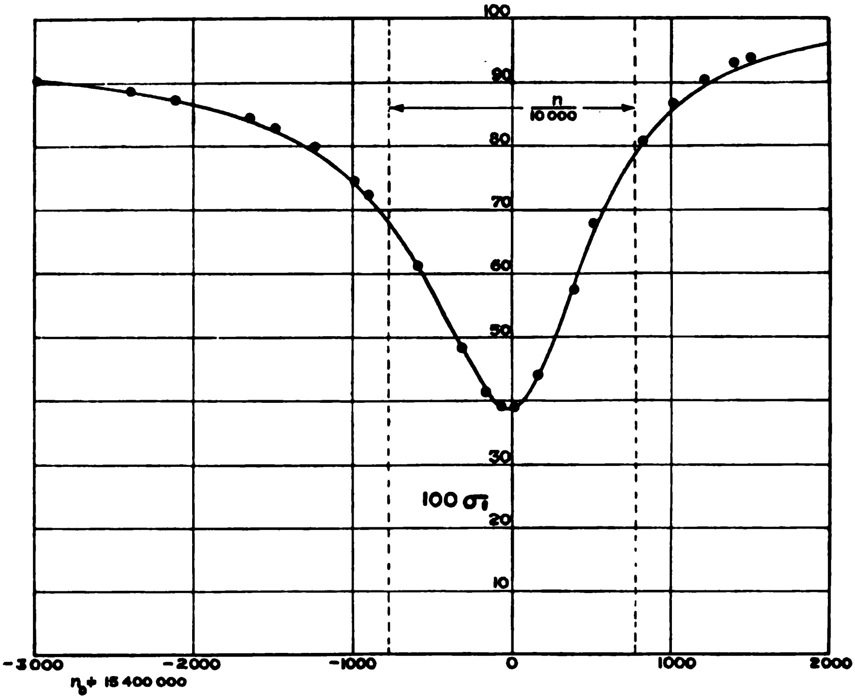


FIG. 9.—RESPONSE CREVASSE FOR A VERY HIGH FREQUENCY TRANSVERSE RESONATOR.

Even at such a frequency the agreement between theory—(drawn curve)—and experiment—(dots in circles)—is satisfactory. In such a case the precise adjustment of the electrical circuit to resonance at the bottom of the crevasse is almost impossible owing to the smallness of the inductance and the capacity. The case shown is one in which the electrical circuit has a resonant frequency somewhat lower than the response frequency of the resonator. The experiments at such frequencies are difficult: special arrangements on the valve oscillator are necessary to enable smooth reversible changes of frequency of uncertainty less than one part in a hundred thousand to be made when the frequency is as high as 15×10^6 (20 metres wavelength).

For all the preceding curves a general form of equation (7*a*) may be used in cases where it is desired merely to plot a curve to see that it fits the points observed. The equation may be written

$$\sigma_1{}^2 = \frac{A^2 + dn^2}{\left[\frac{2dn^2}{n\varphi_1} + Bdn - \frac{A}{\sigma_{1\ \text{min.}}}\right]^2 + \left[dn\left(1 + \frac{2A}{n\varphi_1}\right) + AB\right]^2} \quad . \quad . \quad . \quad . \quad (8)$$

in which $\frac{2}{n\varphi_1}$ belongs only to the electrical circuit, whilst A belongs only to the quartz and is equal to $\frac{n\varphi_2}{2}$. The quantity B depends upon the frequency difference between the electrical circuit and the quartz—whilst $\sigma_{1\text{min.}}$ is determined by the piezo-electric reaction of the quartz upon the electrical circuit.

We have now to consider how we can use equations (7 and 7*a*) and derivations from them in order to evaluate the quantities K, S and K_1.

Determination of $\varphi_2 = SK\omega$.

The quantities which we may vary are (a) ω; (b) $\varphi_1 = RC\omega$ (by addition of resistance in the oscillatory circuit); (c) C; (d) K_2 (by variation of the air gaps). We can observe curves of σ_1, as a function of ω in the way already shown in Figs. 6 to 9 for various known values of φ_1, C and K_2.

By observation of the width of the crevasse in terms of the frequency difference at various chosen values of σ_1 as read off on the plotted curve, we can first determine φ_2 as follows:—

Consider the particular case of (7) when "*dn*"=0. The equation becomes

$$\sigma_1{}^2{}_{\text{min.}} = \frac{\varphi_1{}^2\varphi_2{}^2}{\left[\frac{KK_2{}^2}{CK_t{}^2} + \varphi_1\varphi_2\right]^2 + \left[\frac{K_1K_2\varphi_2}{CK_t}\right]^2} \quad \ldots\ldots\ldots (9)$$

The second term in the denominator is of very small effect on $\sigma_{1\text{ min.}}$ To a first approximation, therefore, we may neglect it. We can then substitute back into equation (7) the term $\varphi_1\varphi_2/\sigma_{1\text{ min.}}$ in place of $\frac{KK_2{}^2}{CK_t{}^2} + \varphi_1\varphi_2$. By confining the attention to that part of the curve corresponding to values of σ_1 not greater than 0·8, terms containing dn^3 and dn^4 may be entirely neglected. On solving for φ_2 it will be found that

$$\varphi_2 = \frac{2dn\sigma_{1\text{ min.}}}{n}\sqrt{\frac{1-\sigma_1{}^2}{\sigma_1{}^2 - \sigma_{\text{min.}}{}^2}}\left\{1 + \tfrac{1}{2}\frac{\sigma_1{}^2}{1-\sigma_1{}^2} \cdot \frac{K_2{}^2}{\varphi_1{}^2K_t{}^2}\left(\frac{2K}{C} - \frac{K_1{}^2}{C^2} + \frac{nKK_1K_2}{dnC^2K_t}\right)\right\} \quad . \quad (10)$$

The terms in the round brackets are correction terms.

Now this equation may be written in the form

$$\varphi_2 = f[\sigma_1][dn] - f'[\sigma_1] \quad \ldots\ldots\ldots\ldots (11)$$

in which $f'(\sigma_1)$ is a small quantity compared with $f[\sigma_1][dn]$. But φ_2 is also positive when "*dn*" is negative and has a value, say, "*dn'*." Measuring dn' to the left, therefore, we have

$$\varphi_2 = f[\sigma_1][dn'] + f'[\sigma_1] \quad \ldots\ldots\ldots\ldots (12)$$

If, therefore, we measure the frequency difference $\delta n = dn + dn'$ right across the crevasse as shown in Fig. 10 at the level, **AB** corresponding to any chosen value of σ_1, we shall have

$$2\varphi_2 = f[\sigma_1][\delta n] \quad \ldots\ldots\ldots\ldots (13)$$

The equation for φ_2 then becomes

$$\varphi_2=\frac{\delta n\sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}}\left\{1+\tfrac{1}{2}\frac{\sigma_1^2}{1-\sigma_1^2}\cdot\frac{K_2^2}{\varphi_1^2K_t^2}\left(\frac{2K}{C}-\frac{K_1^2}{C^2}\right)\right\} \quad . \; . \; . \quad (14)$$

In this equation K and K_1 are unknown, but as they only occur in a correction term of the order of 1 per cent. or 2 per cent., we may assume a value for K_1 based on a value of 4 for the dielectric constant of quartz. The quantity K (as yet unknown) can be eliminated by substitution of its equivalent in the approximate form of equation (8). This gives

$$\varphi_2=\frac{\delta n\sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}}\left\{1+\tfrac{1}{2}\frac{\sigma_1^2}{\varphi_2(1-\sigma_1^2)}\left(\frac{1-\sigma_m}{\sigma_m}\varphi_1\varphi_2-\frac{K_1^2K_2^2}{2C^2K_t^2}\right)\right\} \quad . \; . \; . \quad (15)$$

This equation gives a very accurate measure of φ_2 from observations of δn read off at various values of σ_1 from the curve.

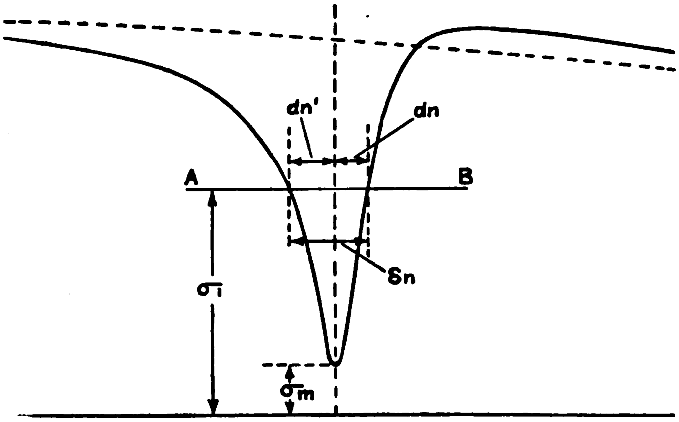


FIG. 10.—DIAGRAMMATIC REPRESENTATION OF A RESPONSE CREVASSE.

For most purposes, however, the correction term may be neglected and the very simple expression (16) used in the determination of φ_2.

$$\varphi_2=\frac{\delta n\sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

In thus determining φ_2 from a curve, the best way is to read off a series of values of δn corresponding to a number of values of σ_1. By plotting $\sqrt{(\sigma_1^2-\sigma_m^2)/(1-\sigma_1^2)}$ as ordinate to δn as abscissa, a straight line should result of slope "m," such that $\varphi_2 \doteqdot \frac{m\sigma_m}{n}$.

As an example of the determination of φ_2 in this manner, the curve Fig. 11 has been plotted for the case of the curve of which the experimental points are given in Fig. 7. It will be seen that the points lie on a very good line. The value of φ_2 obtained from the line is $29{\cdot}7\times10^{-6}$ whence the logarithmic decrement of the quartz $=\pi\times29{\cdot}7\times10^{-6}=0{\cdot}93\times10^{-4}$.

The measurement of φ_2 constitutes the most important single measurement that can be made on a quartz resonator.

Having determined φ_2 we are in a position to reproduce mathematically any curve for a resonator and a circuit in which φ_1 is known, without further analysis. This is seen from the generalised equation (8) which, except for the quantity B, does not entail any knowledge of the resonator other than its damping. The term B only enters into the equation in so far as it effects the symmetry of the curve. It has been seen already by equation (7*a*) that B is very largely dependent upon the small difference between the resonant frequencies of the resonator and the electrical circuits. The deduction of B from the asymmetry of the curve cannot, therefore, safely be used for the purpose of further analysing the resonator circuit.

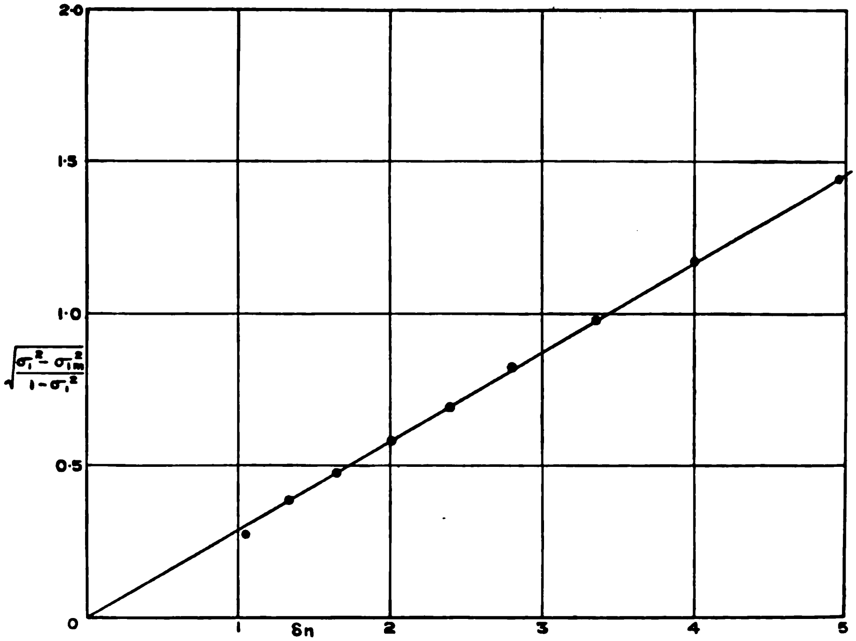


FIG. 11.—LINEAR RELATIONSHIP DEDUCED FROM CREVASSE WHEREBY THE LOG. DEC. OF A RESONATOR MAY BE OBTAINED.

We are therefore left with $\sigma_{1\ \text{min.}}$ only, as a particular property of the observed curve, as a means whereby a further analysis may be made.

Returning to equation (9) in its simplified form, we have, to a close approximation

$$\sigma_{1\ \text{min.}} \doteqdot \frac{\varphi_1\varphi_2}{\frac{KK_2{}^2}{CK_t{}^2} + \varphi_1\varphi_2} \quad \ldots\ldots\ldots\ldots \quad (17)$$

By substitution of $SK\omega$ for φ_2 we can eliminate the unknown quantity K and obtain the equation

$$\sqrt{\frac{\sigma_{1m}}{1-\sigma_{1m}}} = \sqrt{\varphi_1 SC\omega\left(1+\frac{K_1}{K_2}\right)} \quad \ldots\ldots\ldots \quad (18)$$

The quantities we can vary are :—

K_2 by adjustment of the air gaps to known values.

$\varphi_1 = RC\omega$ by addition of resistance in the oscillatory circuit.

C by choice of capacity and inductance in the oscillatory circuit.

Since C and φ_1 occur in exactly the same way in the equation, nothing is gained by varying more than one of them. In practice it is much easier to vary φ_1, since this does not necessitate retuning and does not react on C.

If a series of curves of σ_1 are taken for various values of K_2, and also with various added resistances in the oscillatory circuit we can observe the following quantities on these curves :—

(*a*) The various values of φ_2.
(*b*) The various values of $\sigma_{1\,\text{min.}}$
(*c*) The frequencies at which the various values of $\sigma_{1\,\text{min.}}$ occur.

Observations (*a*) tell us whether the logarithmic decrement of the resonator is independent of the conditions under which it resonates.

Observations (*c*) will be dealt with later, as they give peculiar results which will repay further investigation.

From observations (*b*) we can find S and K_1 by means of equation (18).

Since φ_2 is also known, we can determine K. Finally, N is determined from the relation $NK\omega^2 = 1$.

The procedure is to obtain a family of curves each corresponding to a known air gap, and hence known value of K_2. The values of $\sigma_{1\,\text{min.}}$ are then read off. In carrying out these observations it is, of course, not really necessary to obtain the whole of the crevasse, but by way of illustration a family of curves has been taken. Such a family is shown in Fig. 12. These are fairly complete, and enable a number of interesting facts to be seen. In order to avoid confusion, the observed points have been omitted. The curves are experimental, and not theoretical.

Each crevasse corresponds to a particular air gap, and this is the only quantity which has been varied, except for the small change in C necessary to establish resonance in the electrical circuit at each frequency of response.

It will be seen that the frequency of response increases regularly as the air gap is increased, as indicated by the theory represented in Fig. 4. The values of $\sigma_{1\,\text{min.}}$ also lie on a smooth curve representing a reduced effect upon the oscillatory circuit as the air gap is increased.

It has been necessary to draw these curves on a rather compressed scale of frequency owing to the relatively large changes in response frequency with change in air-gap.

From observations made on each curve when drawn on a more open scale the value of φ_2 was deduced.

φ_2 was found to vary somewhat irregularly, as will be seen by reference to the table on Fig. 12, giving this quantity for the various crevasses. There seems to be a slight increase in φ_2 as the air gap is diminished, but this is not regular. It was afterwards found to be due to variations in either the mounting of the resonator or of the humidity of the air.

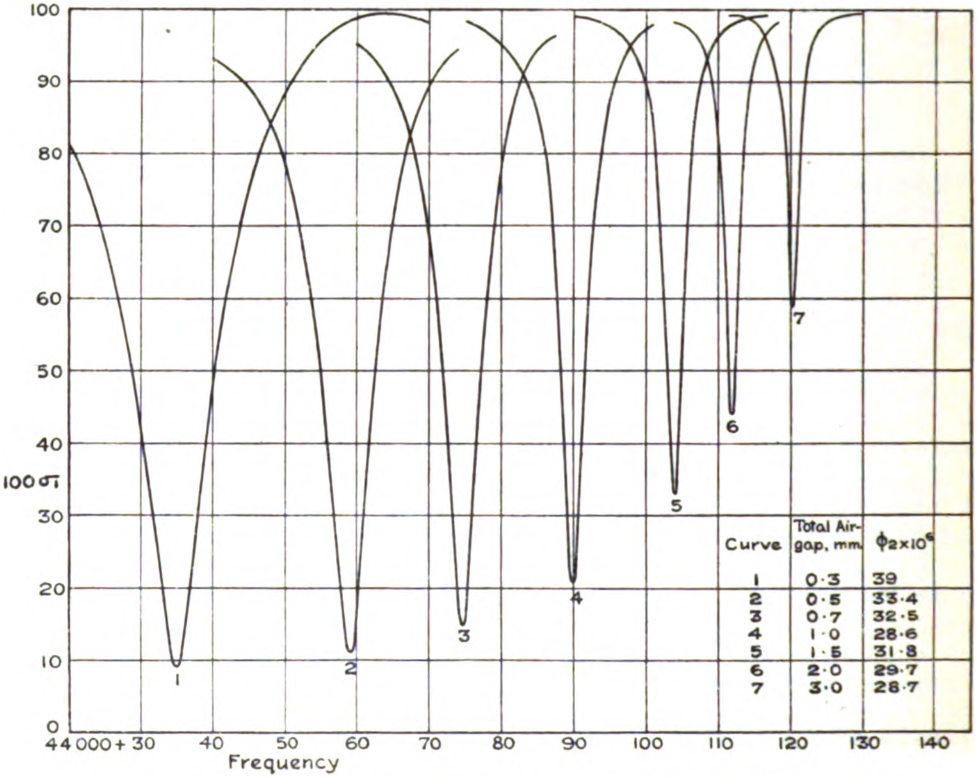
In a later series only a small portion of the crevasse near $\sigma_{1\,\text{min.}}$ was taken, so that all the necessary observations might be made on one occasion. The mounted resonator was placed in a bell jar and kept dry during this series of observations.

Returning now to equation (18), we can write this in the form

$$\sqrt{\frac{\sigma_{1\,\mathrm{min.}}}{1-\sigma_{1\,\mathrm{min.}}}}=A_1+\frac{A_1K_1}{K_2} \quad \ldots\ldots\ldots\ldots \quad (18a)$$

where $A_1=\sqrt{\varphi_1 SC\omega}=\sqrt{RSC^2\omega^2}$.

It will be seen that on plotting $\sqrt{\frac{\sigma_{1\,\mathrm{min.}}}{1-\sigma_{1\,\mathrm{min.}}}}$ as ordinate against $\frac{1}{K_2}$ as abscissa we should obtain a straight line.



Curve	Total Air-gap, mm.	$\phi_2 \times 10^6$
1	0·3	39
2	0·5	33·4
3	0·7	32·5
4	1·0	28·6
5	1·5	31·8
6	2·0	29·7
7	3·0	28·7

FIG. 12.—FAMILY OF CREVASSES SHOWING EFFECT OF VARIOUS AIR GAPS.

It is obvious from the equation that when $\frac{1}{K_2}$ has the extrapolated imaginary value of $-\frac{1}{K_1}$ the left-hand side of (18) becomes zero. The intersection of the line on the axis of $\frac{1}{K_2}$ gives us therefore $-\frac{1}{K_1}$, and hence K_1.

Again, when $K_2=\propto$, and hence $\frac{1}{K_2}=0$, we have $\sqrt{\frac{\sigma_{1\,\mathrm{min.}}}{1-\sigma_{1\,\mathrm{min.}}}}=A_1$. The intercept of the line on the ordinate axis therefore gives us $A_1=\sqrt{\varphi_1 SC\omega}$. Assuming that we have measured the effective resistance of the oscillatory circuit, we can calculate φ_1. Of the other terms, C and ω are known, and hence S may be determined.

The slope of the line is equal to A_1K_1. By choosing another value of φ_1—by inserting a known resistance in the oscillatory circuit—another family of curves of σ_1 can be obtained, and from it a second straight line satisfying equation (18) may be deduced. This line should have a slope proportional to $\sqrt{\varphi_1}$, and should confirm by its intercept on the axis of $\frac{1}{K_2}$ the value of $\frac{1}{K_1}$ obtained by the previous line.

A confirmation of both S and K_1 with respect to variation of air gap and of φ_1 may therefore be obtained by observing several series of crevasses, each crevasse in a series corresponding to a known air-gap and each series corresponding to a chosen value of φ_1. The deduced lines of equation (18*a*) should all meet at the point corresponding to $\frac{1}{K_1}$, and their intercepts on the ordinate axis should be proportional to $\sqrt{\varphi_1}$ if S has remained constant.

An overall average value of S may therefore be obtained by plotting the (intercepts)^2 against φ_1, when a line will be obtained whose slope is equal to $SC^2\omega^2$.

An alternative method of dealing with equation (13) when deducing S and K_1 is to consider it in the form

$$\frac{\sigma_{1\,\mathrm{min.}}}{1-\sigma_{1\,\mathrm{min.}}}=RSC^2\omega^2\frac{K_t^2}{K_2^2} \quad \ldots\ldots\ldots\ldots \quad (19)$$

By plotting $\frac{\sigma_{1m}}{1-\sigma_{1m}}$ against R or against "added R" in the oscillatory circuit we can get a series of straight lines each corresponding to a constant value of K_2. These lines should, in the "added R" case, intersect on the axis of—"added R"—at a point $-R_0$, where R_0 is the effective resistance of the oscillatory circuit when "added R"$=0$.

The slopes of the lines are equal to

$$SK_2^2C^2\omega^2/K_t^2=F^2SK_2^2/K_t^2=m_1 \quad \ldots\ldots \quad (20)$$

where $$F=C^2\omega^2.$$

If, therefore, we plot $\sqrt{m_1}$ against $\frac{1}{K_2}$ as before, we shall obtain the intercept giving K_1 and that giving S. The latter does not now involve φ_1, but only C and ω, and the method averages all the observations.

The foregoing methods of analysis have been applied to a number of resonators. The resonator for which the family of curves of σ_1 is shown in Fig. 12 has been completely analysed in this manner.

Three sets of curves similar to those of Fig. 12 were taken for three different total resistances in the oscillatory circuit. The values of $\sqrt{\frac{\sigma_{1m}}{1-\sigma_{1m}}}$ were evaluated in each set at the corresponding values of K_2 and the resulting lines plotted in accordance with equation (18).

These lines are given in Fig. 13. The lines are the best straight lines through the points observed—shown as dots in circles.

A considerable number of points were taken in each case. It will be seen that the points lie on the lines to a good approximation, and that the lines converge with very good agreement to a point of intersection on the abscissa axis.

The data respecting these lines is given in the following table :—

Table I.—*Resonator.*

Bar 6·22 cms. long by 0·15 cm. thick (direction of electric axis) by 0·75 cm. deep (optic axis). Vibrating in its fundamental longitudinal mode.

Curve.	Total Resistance in Oscillatory Circuit.	φ_1	Intercept OY	S ohms.	K_1 $\mu\mu F$
A	34·2	$6{\cdot}2 \times 10^{-2}$	0·43	1,650	8·7
B	19·3	$3{\cdot}48 \times 10^{-2}$	0·320	1,635	8·7
C	9·4	$1{\cdot}70 \times 10^{-2}$	0·224	1,640	8·7
D	4·70	$0{\cdot}85 \times 10^{-2}$	0·19	2,360	8·7

It will be seen that in the case of lines A, B, C, the value of S is constant to within less than 1 per cent.

Line D was taken afterwards in order to bring out a special point.

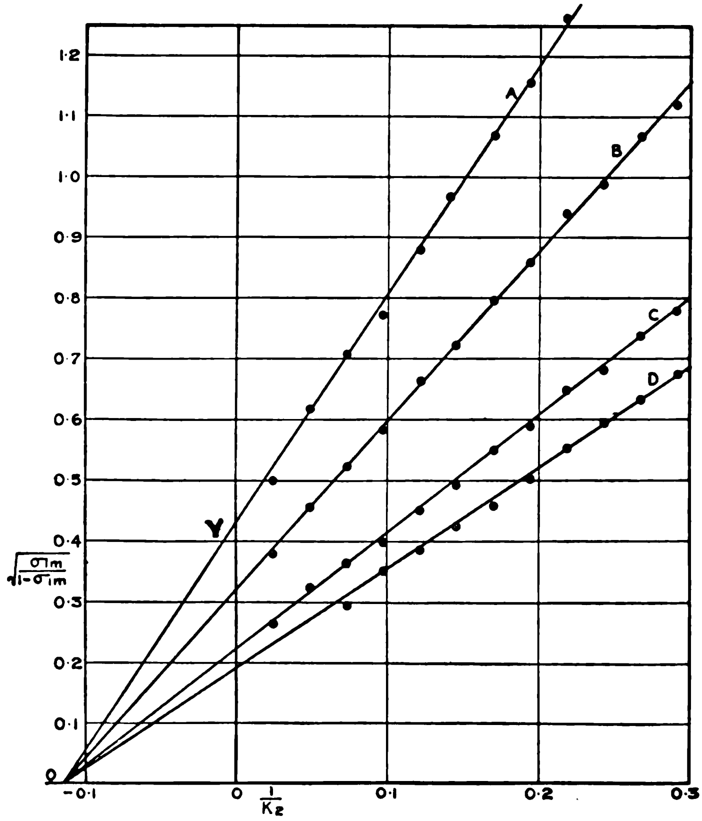


Fig. 13.—Linear Relationship obtained from Fig. 12 whereby the Resonator Network may be analysed.

It was soon found in these experiments that the damping was variable from day to day. This was found to be due to two causes. (*a*) The mode of support, and (*b*) the state of the surface of the resonator with respect to cleanness and dryness.

The experiments resulting in lines A, B and C were very carefully carried out. The resonator, after careful cleaning, was placed in an air-tight enclosure, and dry air was pumped through it after each adjustment had been made to the resonator.

The experiments D were carried out without the enclosure and on a damp day. The increase in S is very marked, and is probably largely due to an increase in the electrical losses on the surface of the quartz. It will be observed that the line passes through the same value of K_1, showing that this constant does not appear to be affected by the moisture in the air.

In order that these particular experiments might be carried through in a single series, attention was concentrated upon observations of $\sigma_{1\,\text{min.}}$, and not on the delineation of the whole of the σ_1 curve. Consequently, values of φ_2 for these actual conditions were not obtained. If, however, the evidence of the tests made in moist air is taken for the purpose of the assumption that K_1 is not dependent on φ_2, we can make use of any of the curves of σ_1 taken at any time notwithstanding φ_2, and hence S may be different for different curves. We can do this, of course, because K_1 may be considered as known and constant in equation (8). For the purpose of obtaining K the equation takes the convenient form

$$K=\varphi_1\varphi_2 C\left(1+\frac{K_1}{K_2}\right)^2\left(\frac{1-\sigma_{1m}}{\sigma_{1m}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Using this equation on about 15 different curves of σ_1 for cases in which φ_1, φ_2 and K_2 have each been varied over wide ranges, results have been obtained as shown in Table II.

TABLE II.—*Longitudinal Resonator—Fundamental Mode of Vibration at* 44,000 ∾ *per second. Dimensions*—6·22 *cm. long,* 0·15 *cm. thick,* 0·75 *cm. deep.*

Total Air Gap, mm.	K_2 $\mu\mu F$	φ_1	φ_2	$\sigma_{1\,\text{min.}}$	$K\,\mu\mu F$
0·3	$13{\cdot}7_3$	$8{\cdot}7\times10^{-3}$	$41{\cdot}0_8\times10^{-6}$	$0{\cdot}09_0$	0·0630
0·3	$13{\cdot}7_3$	$17{\cdot}0\times10^{-3}$	$41{\cdot}0_4\times10^{-6}$	$0{\cdot}17_4$	$0{\cdot}058_1$
0·3	$13{\cdot}7_3$	$8{\cdot}5\times10^{-3}$	$39{\cdot}0_0\times10^{-6}$	$0{\cdot}09_1$	$0{\cdot}057_7$
0·5	$8{\cdot}2_4$	$8{\cdot}5\times10^{-3}$	$33{\cdot}0_4\times10^{-6}$	$0{\cdot}11_0$	$0{\cdot}063_2$
0·5	$8{\cdot}2_4$	$20{\cdot}6\times10^{-3}$	$31{\cdot}0_3\times10^{-6}$	$0{\cdot}19_8$	$0{\cdot}059_5$
0·7	5·8	$8{\cdot}5\times10^{-3}$	$32{\cdot}0_5\times10^{-6}$	$0{\cdot}15_0$	$0{\cdot}062_8$
0·7	5·8	$8{\cdot}7\times10^{-3}$	$40{\cdot}0_3\times10^{-6}$	$0{\cdot}18_6$	$0{\cdot}061_5$
1·0	$4{\cdot}1_2$	$8{\cdot}5\times10^{-3}$	$28{\cdot}0_6\times10^{-6}$	$0{\cdot}20_9$	$0{\cdot}058_2$
1·0	$4{\cdot}1_2$	$8{\cdot}7\times10^{-3}$	$40{\cdot}0_2\times10^{-6}$	$0{\cdot}26_9$	$0{\cdot}060_0$
1·0	$4{\cdot}1_2$	$20{\cdot}6\times10^{-3}$	$27{\cdot}0_2\times10^{-6}$	$0{\cdot}37_0$	$0{\cdot}060_5$
1·5	2·75	$8{\cdot}5\times10^{-3}$	$31{\cdot}8\times10^{-6}$	$0{\cdot}33_0$	0·0618
1·5	2·75	$8{\cdot}7\times10^{-3}$	$40{\cdot}6\times10^{-6}$	$0{\cdot}40_7$	$0{\cdot}058_3$
2·0	$2{\cdot}0_6$	$8{\cdot}5\times10^{-3}$	$29{\cdot}7\times10^{-6}$	$0{\cdot}44_0$	$0{\cdot}057_3$
3·0	1·37	$8{\cdot}5\times10^{-3}$	$28{\cdot}7\times10^{-6}$	0·588	0·0602
3·0	1·37	$8{\cdot}7\times10^{-3}$	$44{\cdot}0\times10^{-6}$	$0{\cdot}68_3$	$0{\cdot}062_4$
			Average value	... ...	0·0603
	Mean variation from mean = 2·7 per cent.				

The foregoing analysis applies to a longitudinal resonator. It is interesting to see whether the same general agreement with theory may be obtained in the case of a piece of quartz vibrating transversely.

A similar set of experiments was, therefore, carried out on the small rectangular piece for which a specimen curve of σ_1 has been given in Fig. 8.

A suitable gap was constructed from an ordinary 25 mm. micrometer gauge, and a careful series of curves of σ_1 for various air gaps and for various values of φ_1 were taken as before.

As will appear later on, remarkable results are obtained with transversely vibrating resonators under certain adjustments of the air gap. The series of curves was specially chosen in the light of this experience. This explains the apparently irregular air gaps chosen. The results of these experiments are shown in Fig. 14.

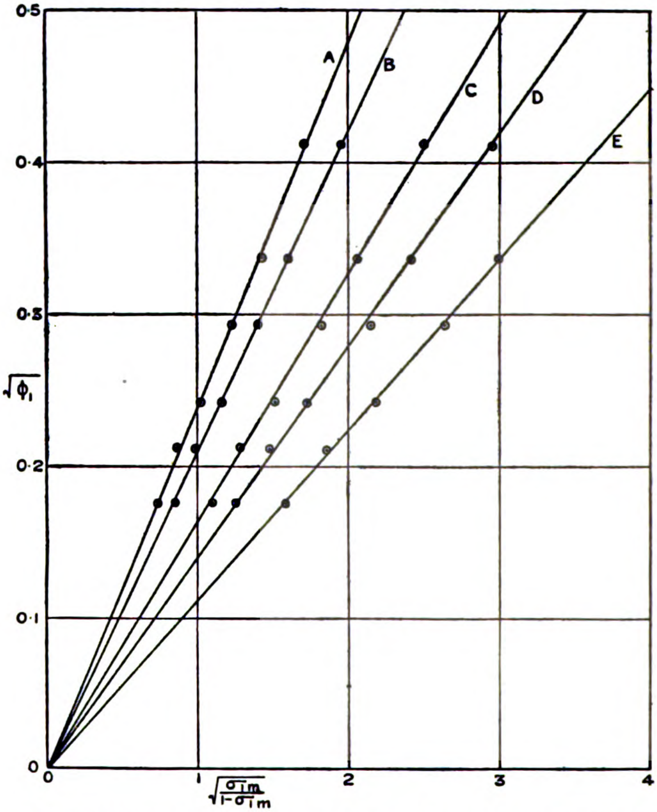


FIG. 14.—LINEAR RELATIONSHIP AS A FUNCTION OF THE LOG. DEC. OF THE OSCILLATORY CIRCUIT.

By way of variation, the lines have been plotted in accordance with equation (19). Thus, taking square roots of each side, $\sqrt{\sigma_{1m}/1-\sigma_{1m}}$—has been plotted as ordinate to an abscissa which is a fraction of the total resistance in the circuit. Actually the quantity plotted is $\sqrt{\varphi_1}$.

Each line A, B, C, etc., now corresponds to a definite air gap. The points on the line are obtained from calculation made from the observation of the values of $\sigma_{1\,\mathrm{min.}}$ obtained for various values of added resistance to the oscillatory circuit. By the help of the measurement of the effective resistance of the circuit when no resistance is added the value of φ_1 was calculated in each case.

The lines of Fig. 14 correspond in order to air gaps of 0·2, 0·4, 0·9, 1·2 and 1·8 mm., for which the capacities K_2 are 11·35, 5·67, 2·52, 1·88 and 1·26$\mu\mu$F respectively.

It will be seen that good proportionality exists between φ_1 and $\sigma_{1m}/1-\sigma_{1m}$.

The slopes of these lines gives us a quantity m_2, such that

$$m_2=\sqrt{\sigma_{1m}/\varphi_1(1-\sigma_{1m})}=(1+K_1/K_2)\sqrt{\varphi_2 C/K}.$$

It will be seen that on plotting m_2 against $1/K_2$ we shall get a mean line similar to those of Fig. 13.

The necessary measurement of φ_2 for each air gap was carried out for the condition "added R"$=0$. The values obtained varied considerably, and appeared to diminish with increasing air gap. In the light of much more careful experiments made to investigate the effects of air gap on damping, remarkable effects were obtained, and for this series of experiments it is probable that an average of the values of φ_2 represents more nearly the truth than the assumption that the values obtained are each correct.

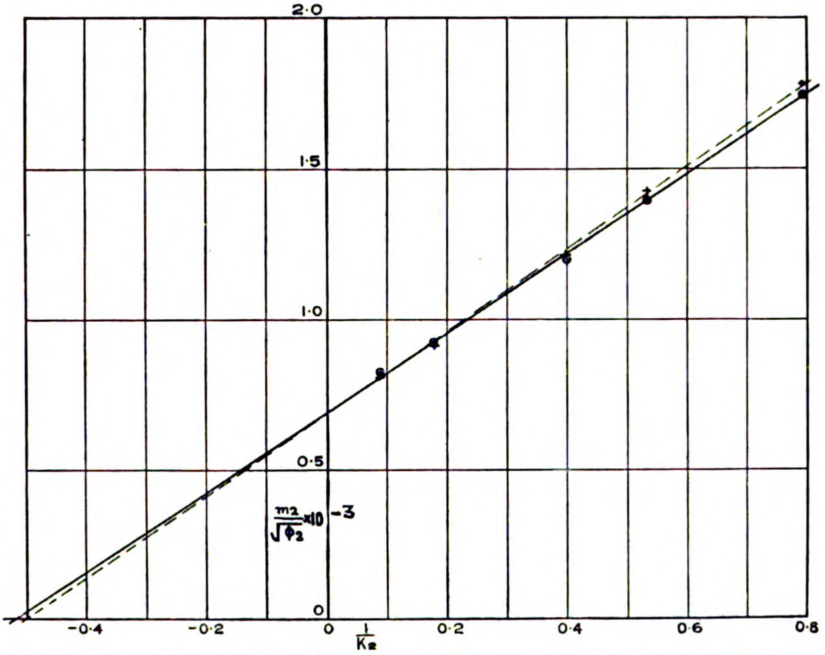


FIG. 15.—ANALYSIS OF RESONATOR NETWORK FROM OBSERVATIONS ON THE LINES OF FIG. 14.

In order of increasing air gap they were $\varphi_2=27{\cdot}1$, $26{\cdot}7$, $25{\cdot}6$, $25{\cdot}0$ and $24{\cdot}0\times10^{-6}$ in each case.

The line of Fig. 15 represents the values of $m_2/\sqrt{\varphi_2}$ plotted against $1/K_2$. The intercept on the axis $m_2/\sqrt{\varphi_2}$ gives $\sqrt{C/K}$, from which K is determined. The intercept on the axis of $1/K_2$ gives $-\frac{1}{K_1}$. From the line the actual values are $K=0{\cdot}0041\mu\mu$F and $K_1=1{\cdot}93\mu\mu$F. If the observed values of φ_2 are used the dotted line is obtained which appears to be slightly steeper and gives for K and K_1, the values $0{\cdot}0041\mu\mu$F and $2{\cdot}00\mu\mu$F respectively.

Effect of Air Gap on Frequency.

We have seen in the simple circle diagram of the resonator that according to the theory the response frequency is a different quantity from what has been defined as the true resonant frequency—i.e., that frequency at which $NK\omega_0^2=1$.

We have seen that the response frequency at which σ_1 has its minimum value occurs to a very close approximation, when the effective capacity K_0 of the resonator mesh is equal to $-K_2$. As already noted in equation (4) this means that $\sigma_{1\text{min.}}$ occurs when $q=-\frac{K}{K_1+K_2}$.

We have, therefore, $1-NK\omega^2 \doteqdot 2(n_0-n)/n_0$ for any value of n near n_0.

This gives the relation

$$\underset{[\sigma_{1\text{min.}}]}{n}=n_0+n_0K/2(K_1+K_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

where $\underset{[\sigma_{1\text{min.}}]}{n}$ is the frequency at which σ_1 has its minimum value.

By observation of $\underset{[\sigma_{1\text{min.}}]}{n}$ at various values of K_2 we ought, therefore, to obtain a check on the value of K or to discover whether K varies slightly with air gap.

Using the determined value of K_1 we can plot $\underset{[\sigma_{1\text{min.}}]}{n}$ against $\frac{1}{K_1+K_2}$. A straight line should result having a slope $n_0K/2$, and an intercept, where $\frac{1}{K_1+K_2}=0$, at which point $n=n_0$.

A great number of measurements of the response frequency have been made, on various resonators as a function of air gap, and a number of very interesting results have been obtained.

A typical case is given in the curve of Fig. 16 for the longitudinal resonator of which the analysis has already been given. The values of response frequency are plotted against the corresponding values of $1/(K_1+K_2)$. For this purpose the value $8{\cdot}7\mu\mu$F already determined has been used for K_1.

The vertical dotted line represents the case for an infinite air gap, for which $K_2=0$, and hence gives a limiting value beyond which n cannot rise.

A thin line of slope to fit the equation $\frac{2dn}{n}=\frac{K}{K_t}$ has been drawn to pass through the point A on the experimental curve. Values of $0{\cdot}0603\mu\mu$F and $8{\cdot}7\mu\mu$F respectively have been used for K and K_1 in calculating this line.

It is seen that the frequency change does not accurately obey the simple theory, but that it tends to do so for large air gaps, where it is practically coincident with the line.

Cady has already indicated that a change of resonant frequency of a bar is to to be expected when the air gap is varied, and suggests that this is due to the leakage electric field resulting from the vibration of the bar. The suggestion is that the vibrating bar is analogous to a bar magnet, and that the leakage field reacts upon the modulus of elasticity thus altering the true resonant frequency.

It is probable that this reasoning is true in part, but it is only necessary to assume it in respect of the departure of the experimental values of n from those corresponding to the straight line of slope $Kn_0/2$, and must not be considered as the main cause of the frequency change.

It may be quite definitely stated that, except for very small air gaps (less than 0·1 mm.) the main change in frequency consequent upon an alteration in the air-gap is due to the fact that the resonator behaves as an inductance of such value as to give the equivalent electrical resonance corresponding to the capacity K_2 of the air gap.

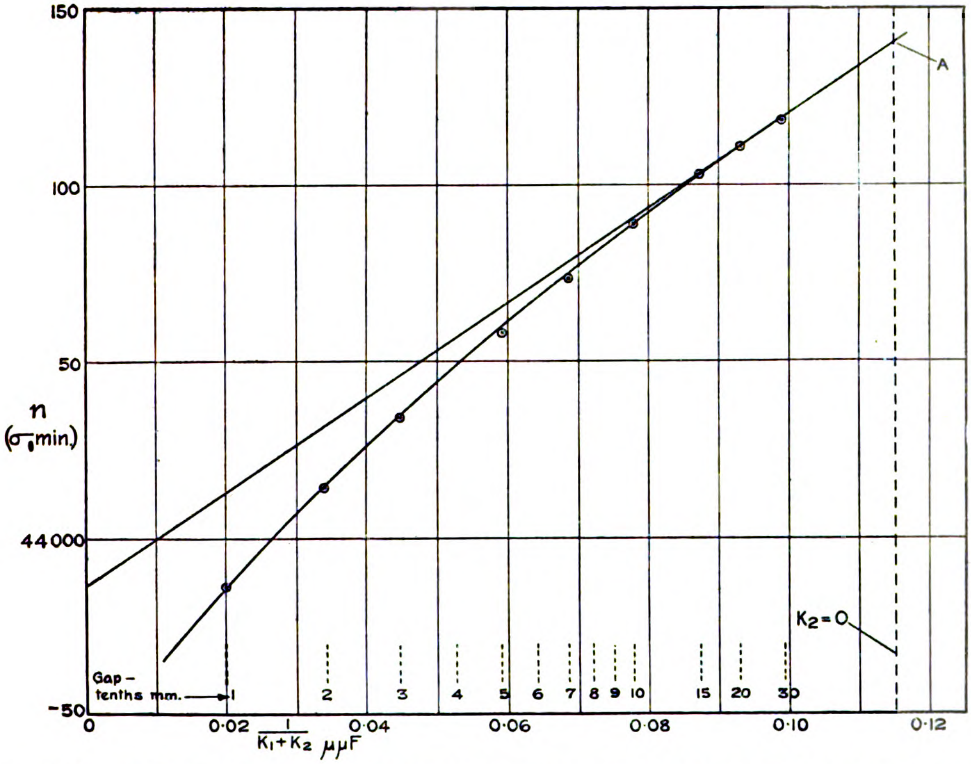


FIG. 16.—VARIATION OF RESPONSE FREQUENCY WITH VARIATION OF AIR GAP FOR A LONGITUDINAL RESONATOR.

This is a very interesting fact, and requires further experimenting, using electrodes of smaller length than that of the bar, with a view to the experimental determination of the real change in the true resonant frequency as a function of air gap.

It will be seen that the possible change in frequency is by no means negligible on a resonator if the air gap changes adventitiously. On the other hand, such a possibility of variation affords a convenient means of finely adjusting the frequency to a desired value when once the resonator has been ground to within one or two parts in a thousand in frequency. There is a range of about three parts in a thousand in a longitudinal resonator for reasonable limits of the air gap.

To a sufficient approximation the change in frequency produced by an increase in air gap from a total of t_1 to t_2 will be given by the expression

$$\frac{\Delta n}{n}=\frac{kt}{2\mu}\left[\frac{t_2-t_1}{(kt_1+t)(kt_2+t)}\right]$$

where t is the thickness of the quartz,
k is its dielectric constant (approx. 4·3),
and μ is the piezo-electric ratio K_1/K.

For an average good specimen this quantity is of the order 150 for the transverse effect which produces the longitudinal force. For a good plate vibrating transversely the value of μ is of the order 400 to 500. In the case of a resonator vibrating transversely remarkable effects are obtained when the air gap is varied.

Take, for example, the transverse resonator for which the analysis has been given. For a narrow range of air gap extending from a very small total gap up to one of a few tenths of a millimetre, the change in frequency is smooth and of the same general character as that shown by the longitudinal resonator. The increase in $\sigma_{1\,\text{min.}}$ is also smooth and of the rate to be expected.

At certain air gaps, however, the behaviour is found to be quite rapidly variable. The frequency changes suddenly become negative, and then positive again within quite narrow ranges of air gap. The values of $\sigma_{1\,\text{min.}}$ also show corresponding fluctuations. These effects when first noted strongly suggested further subsidiary resonance phenomena.

Further series of measurements were, therefore, taken with extraordinary care. The micrometer air gap within which the piece of quartz was supported shown in Fig. 32, was found to be uncertain in its action owing to want of parallelness between the plane faces of the electrodes, consequent upon these being not quite perpendicular to the axis of the micrometer screw.

This was a difficult matter to correct, as it is not easy to adjust a plane face 3 cm. in diameter to be so nearly perpendicular to the axis of the micrometer screw that the air gap remains parallel to an accuracy of 0·002 mm. over the whole face for any setting.

After a good deal of adjustment it is believed that this degree of accuracy was attained and the final series of readings was taken.

The readings taken were those of $\sigma_{1\,\text{min.}}$ and frequency for successive changes of 0·02 mm. in air gap on each side over most of the range and for changes of 0·01mm. over certain parts of the range.

The remarkable curves obtained are shown in Figs. 17 and 18. The upper curve gives the variation of frequency with variation in air gap and the lower curve gives the corresponding changes in $\sigma_{1\,\text{min.}}$ Both curves have been plotted to the same scale of air gap and not to a scale of $1/(K_1+K_2)$ as in Fig. 16. The scale represents total air gap, i.e., a reading of 1·0 mm. means that the gap was 0·5 mm. on each side of the resonator. In order to obtain these curves the utmost care was necessary to ensure that the two air gaps were precisely equal. The equality necessary was certainly to less than 0·01 mm. and was difficult to obtain.

It will be seen that a large increase in the apparent damping and a corresponding

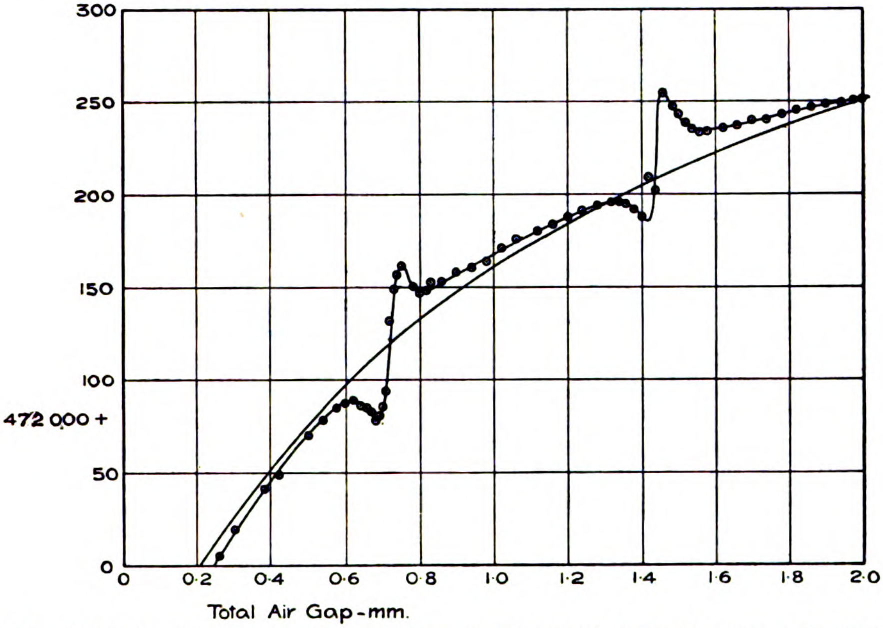


FIG. 17.—VARIATION OF RESPONSE FREQUENCY WITH VARIATION OF AIR GAP FOR A TRANSVERSE RESONATOR.

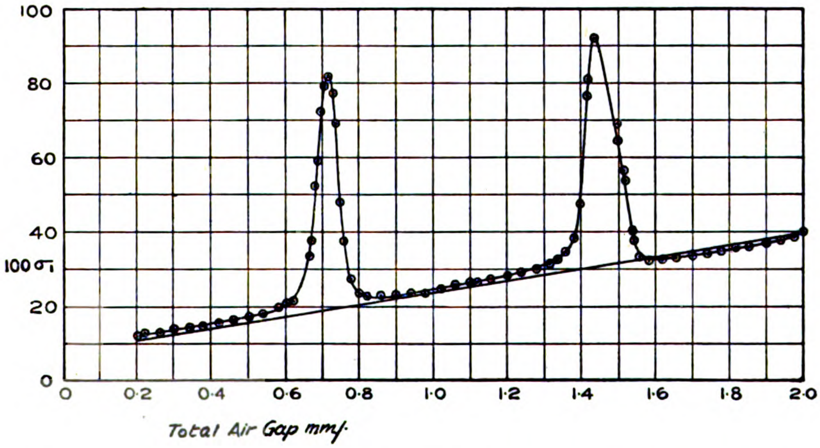


FIG. 18.—VARIATION OF DAMPING COEFFICIENT CORRESPONDING TO FIG. 17.

fluctuation in the frequency of $\sigma_{1\,\text{min.}}$ occurs at air gaps of 0·72 and 1·44 mm., representing gaps on each side of 0·36 and 0·72 mm. respectively.

Now the shape of the two effects suggests immediately to those familiar with coupled circuits that the equivalent of a coupled resonant circuit is operating. There is no doubt that this is the case and that the effect is due to resonance of the plate of air between the surface of the quartz and the electrode.

The effect recurs every time the air gap has a value which is an integral multiple of the half wavelength of the supersonic air wave corresponding to the frequency of the resonator.

Thus, assuming the value for the velocity of sound in air, of 340 metres per second to hold for such high frequency air waves, then, at a frequency of 472,000 vibrations per second the half wavelength is $\frac{340{,}000}{2\times 472{,}000}=0{\cdot}360$ mm., a result in exact accordance with the observed value.

The damping is enormously increased as a result of the greatly augmented air vibrations occurring in the space between the surface of the quartz and the electrode.

The effective value of φ_2 is increased twenty-fold owing to this large absorption of energy from the quartz. Whether the energy is wasted as viscous damping in the air or whether it is radiated as an augmented air wave I am at present unable to say.

The equivalent electrical system will be that of a closed oscillatory circuit coupled inductively to the fictitious inductance N of Fig. 2.

The thin lines on the figures are the values of $\sigma_{1\,\text{min.}}$ and n respectively, which are obtained by calculation using the previously determined values of S, K and K_1.

Except for the regions where the air resonance introduces its reaction the agreement is quite good in view of the difficulty of the experiments.

It will be seen upon reference to the scale of frequency in Fig. 17 that the change in frequency consequent upon a change in air gap is much smaller for this transverse resonator than for the longitudinal resonator previously given.

The total possible change from zero to an infinite air gap is less than one part in a thousand. The horizontal lines of Fig. 17 are spaced apart roughly by one part in ten thousand in frequency. On the scale upon which these results are plotted, therefore, a change of one part in a hundred thousand in frequency is easily seen.

Within close limits, therefore, it may be provisionally stated that the behaviour of a transverse resonator can be imitated closely by an equivalent electrical network, but that at certain values of air gap the resonator behaves as though an additional resonant circuit were coupled to the network representing the resonator. This resonant circuit nust be considered to have a frequency so varied as to be proportional to K_2 and to become equal to that of the resonator at those values of the air gap, which represent integral half wavelengths in air of the frequency of the resonator.

Current in the Resonator Circuit.

The whole of the preceding considerations refer to the effects upon an oscillatory circuit when the resonator is connected in parallel with the condenser forming the capacity of an oscillatory circuit. It has been shown how an analysis of the network may be made from observations of the current in this circuit.

This procedure, though much favoured by the writer, is by no means the only method by which the equivalent constants of the quartz resonator may be obtained.

We have still to consider the current taken by the resonator itself. This is the current I_2 of Fig. 3(*b*). But there are circuits to which the resonator may be connected other than the oscillatory circuit that we have been considering.

It has already been shown that the circuit representing the resonator itself, is one in which all the parts have very high impedance. Thus, we have K of the order $0{\cdot}05\mu\mu F$ for a resonator of frequency of the order 40,000, $\frac{1}{K\omega}$, therefore, is no less than 80×10^6 ohms. K_2 is of the order $5\mu\mu F$ giving an impedance of about 1 megohm. Measurements on such circuits are by no means easy since the currents are very small except at resonance. It is necessary to use a current measuring device of high resistance in order to obtain useful deflections. The presence of this resistance in the circuit has a considerable effect in reducing the current at resonance and increases the apparent decrement of the resonator considerably. By the use of a Duddell thermo-galvanometer with heater of about 100 ohms it is, however, possible to get observations without risk of breaking the quartz or of vitiating the results owing to reaction on the source. Difficulties also arise owing to parasitic currents to earth since earth capacities are by no means small compared with K, K_1 and K_2.

These effects can, however, all be dealt with by a careful attention to the circuit arrangements and by a correct procedure in the treatment of the observations.

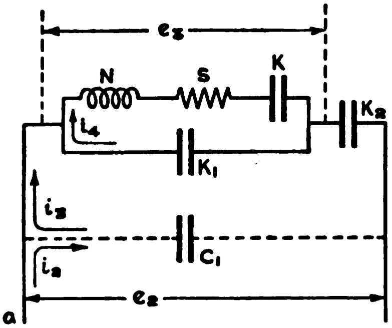


Fig. 19.—Diagram of the Equivalent Network of a Resonator connected to a Condenser.

The cases which may be considered are as follows :—

(1) Constant voltage applied to the terminals of the resonator. Two possibilities arise.

(a) The capacity C_1 of Fig. 19 is small but not negligible compared with K_2. Such a capacity always exists in practice due to leads and earth capacities.

(b) The capacity C_1 is purposely made large, by the use of a condenser, but the voltage e_2 is still considered constant (the use of an inducing coil of a very few turns closely coupled to the source enables this condition to be satisfied).

The second case is :—

(2) The voltage e_2 corresponds to that operating when the resonator is shunted across an approximately tuned resonant circuit.

This is the case used experimentally by Cady and is complicated to deal with algebraically.

Cases (1) (a) and (b) will be taken first. The circuit and conditions are as in Fig. 19. The voltage e_2 is to be considered constant.

The instantaneous current i_2 is that of which the root-mean-square value I_2 is measured by the thermo-galvanometer. The current i_3 is to be considered inaccessible to measurement, but its root-mean-square value is a real quantity; i_4 has no existence as a current but has its counterpart in the mechanical vibration of the resonator.

By connexion of the points *a*, *b*, to a coil of small self inductance and small resistance so that no approach to resonance in the circuit carrying current i_2 occurs, then, the E.M.F. induced in this coil when coupled to a source will remain sensibly constant over the narrow range of frequency concerned.

Experiments under such conditions show that as frequency is smoothly varied, I_2 rises to a sharply defined maximum then falls to a less well defined minimum, and finally approaches asymptotically its original value. The curve is shown in Fig. 20.

It is convenient, from an experimental standpoint, when C_1 is small, to allow the maximum current obtained to be equal to unity and to call the current ratio at any other point σ_2, where $\sigma_2 = I_2/I_{2\,\text{max.}}$.

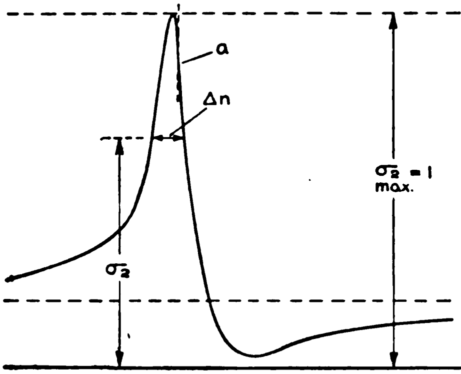


FIG. 20.—CURRENT RESPONSE FREQUENCY CURVE FOR A RESONATOR WITH A SMALL PARASITIC CAPACITY IN PARALLEL.

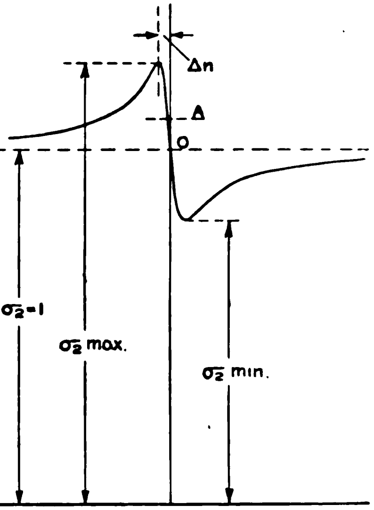


FIG. 21.—THE SAME AS FIG. 20, BUT WITH A RELATIVELY LARGE CAPACITY IN PARALLEL.

When C_1 is large, the curve of σ_2 takes on a more symmetrical form of the type shown in Fig. 21. In this case it is more convenient to choose the scale of deflections such that the value of σ_2 approaches unity outside the range where σ_2 changes rapidly. The maximum and minimum values of σ_2 are then connected by the relation $\sigma_{2\text{max.}} \times \sigma_{2\text{min.}} = 1$. The two equations for σ_2 are as follows :—

(*a*) C_1 small and $\sigma_{2\,\text{max.}}$ chosen equal to unity.

$$\sigma_2{}^2 = \frac{\varphi_2{}^2 + \left[q + \frac{K(C_1+K_2)}{C_1K_t+K_1K_2}\right]^2}{\left[\varphi_2{}^2+\left(q+\frac{K}{K_t}\right)^2\right]\left[1+\frac{K^2K_2{}^4}{K_t{}^2(C_1K_t+K_1K_2)\,\varphi_2{}^2}\right]} \quad \ldots\ldots \quad (22)$$

(*b*) C_1 not small, and $\sigma_{2\,\mathrm{max.}} \times \sigma_{2\,\mathrm{min.}} = 1$.

$$\sigma_2{}^2 = \frac{\varphi_2{}^2 + \left[q + \dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2}\right]^2}{\varphi_2{}^2 + (q+K/K_t)^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

For certain purposes it is convenient to consider as origin of frequency, that value where $q = -K/K_t$ and to write $q = -\dfrac{K}{K_t} - \dfrac{2dn}{n}$.

Equation (22) becomes

$$\sigma_2{}^2 = \frac{n^2\varphi_2{}^2/4 + \left[\dfrac{nKK_2{}^2}{2K_t(C_1K_t+K_1K_2)} - dn\right]^2}{\left(\dfrac{n^2\varphi_2{}^2}{4} + dn^2\right)\left[1 + \dfrac{K^2K_2{}^4}{\varphi_2{}^2K_t{}^2(C_1K_t+K_1K_2)^2}\right]} \quad . \; . \; . \; . \; . \; . \; . \quad (24)$$

In case (*b*), however, it is more convenient to choose an origin of frequency such that q is the mean of $\dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2}$, and $\dfrac{K}{K_t}$. We substitute for q, therefore, the quantity

$$q = -\frac{K}{2}\left[\frac{(C_1+K_2)}{C_1K_t+K_1K_2} + \frac{1}{K_t}\right] - \frac{2dn}{n}.$$

The equation for σ_2 then takes the very convenient form

$$\sigma_2{}^2 = \frac{\dfrac{n^2\varphi_2{}^2}{4} + (D-dn)^2}{\dfrac{n^2\varphi_2{}^2}{4} + (D+dn)^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

where

$$D = \frac{nKK_2{}^2}{4K_t(C_1K_t+K_1K_2)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25a)$$

These equations differ from those previously considered earlier in the Paper in that the point of resonance is not immediately obvious by an inspection of the curves. If we define resonance as the condition such that the current I_3 actually flowing in the quartz circuit is in phase with the voltage applied, then σ_2 corresponding to this frequency may have values varying from the point *a* of Fig. 20 very near $\sigma_{2\,\mathrm{max.}}$ for the curve, where C_1 is small to the point *A* on Fig. 21 very near $\sigma_2 = 1$ for the case where C_1 is large.

We will consider only equation (25) in developing the means of obtaining φ_2 and D.

Differentiating (25) with respect to "*dn*" for max. and min. values of σ_2 it will be found that $\sigma_{2\,\mathrm{max.}}$ and Δn at which it occurs (*see* Fig. 21) are connected by the equation

$$(\sigma_{2\,\mathrm{max.}})^2 = \frac{2\Delta n/n + \sqrt{4\Delta n^2/n^2 - \varphi_2{}^2}}{2\Delta n/n - \sqrt{4\Delta n^2/n^2 - \varphi_2{}^2}} \quad . \; . \; . \; . \; . \; . \; . \quad (26)$$

From this equation it is found that

$$\varphi_2 = \frac{4\Delta n}{n} \cdot \frac{\sigma_{2\mathrm{max.}}}{\sigma_2{}^2{}_{\mathrm{max.}} + 1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (27)$$

By substitution of φ_2 and $\sigma_{2\,\text{max.}}$ into equation (25) we find that

$$D=\frac{2\Delta n}{n}\cdot\frac{\sigma_2{}^2{}_{\text{max.}}-1}{\sigma_2{}^2{}_{\text{max.}}+1} \quad \ldots\ldots\ldots\ldots \quad (28)$$

also

$$D=\frac{\varphi_2(\sigma_2{}^2{}_{\text{max.}}-1)}{2\sigma_{2\text{max.}}} \quad \ldots\ldots\ldots\ldots \quad (29)$$

These equations enable φ_2 and the quantity A to be determined from the curve of σ_2.

The determination of K and K_1 can be made by observing a family of curves of σ_2 each corresponding to a chosen air gap and hence known value of K_2.

From these curves, values of A as a function of K_2 may be deduced.

This cannot be done very conveniently for case (*a*) in which C_1 is comparable with K_1, since the base line value of σ_2 is too small to be observed with accuracy. All the curves of σ_2 for various values of K_2 will be nearly similar.

In the case (*b*), however, where C_1 is large compared with K_1 we can write equation (25*a*) for D in the form

$$\frac{1}{\sqrt{D}}=\sqrt{\frac{2C_1}{K}}\left(\frac{K_1}{K_2}+1+\frac{K_1}{2C_1}\right) \quad \ldots\ldots\ldots \quad (30)$$

If, therefore, we plot the experimentally determined values of $\frac{1}{\sqrt{D}}$ obtained by (29) against $\frac{1}{K_2}$ it is seen from equation (30) that a straight line should result from which K and K_1 may be observed.

At the point $\frac{1}{K_2}=0$ the intercept $\frac{1}{\sqrt{D}}$ gives approx. $\sqrt{\frac{2C_1}{K}}$, whence K is determined, since C_1 is known. At the point $\frac{1}{\sqrt{D}}=0$ we have

$$\frac{1}{K_1}=-\left(\frac{1}{K_2}+\frac{1}{2C_1}\right),$$

thus giving K_1, and so analysing the resonator mesh. The measurement of φ_2 by observation of Δn is not very accurate, since this quantity is small, and not too well defined. Also the determination of φ_2 by this relationship only makes use of one point on the curve of σ_2. The curve of σ_2 does not lend itself quite so easily to the development of a straight line of slope proportional to φ_2 in the way already shown for σ_1.

In order to develop such an equation it is convenient and instructive to resort to the vector admittance diagram of the case under consideration—i.e., with the resonator system connected to a condenser across which a constant voltage is maintained.

Fig. 22 gives the vector admittance and conductance relationship for the case concerned. We have already seen that the vector diagram of the simple quartz mesh given by equations (1) and (2) is a circle. A part of this circle has been given in Fig. 4. Suppose, for the moment, that this impedance circle is that partly shown by the dotted arc passing through O_2 and drawn with O_2X_2 as the axis of effective resistance and O_2Y as axis of effective inductance. We set back O_2O_1 along O_2Y equal to $\frac{1}{K_2\omega}$, and draw an axis O_1X_1, cutting this arc in R. Then O_1R is the effective impedance of the mesh, including K_2 at the frequency of maximum response. Now let us change our scales from those of impedance to those of admittance. The effective impedance O_1R is almost exactly equal to the effective resistance S_1 of Fig. 4, and will become an effective conductance. We can choose the scales so that O_2O_1 now becomes the permittance $K_2\omega$. It is a property of the circular impedance diagram that its inverse admittance diagram is also a circle. This circle is shown as O_2TX_2 of diameter equal to $\frac{1}{O_1R}$. We now set out a new axis ON, such that OO_2 is equal to the permittance $C_1\omega$ of the condenser C_1 of Fig. 6. The circle O_2TX_2 is then redrawn at ONP. The construction of the current-frequency curve $O'N'P'$ follows along lines somewhat similar to those already clearly set out in Prof. Mallett's Paper.(8) In the present case the circle is tangential at O. Any vector admittance O_1P is now shown correctly in phase angle and magnitude with respect to OO_1 for a value of σ_2 corresponding to a point P' on the curve $O'N'P'$ at any chosen frequency difference dn.

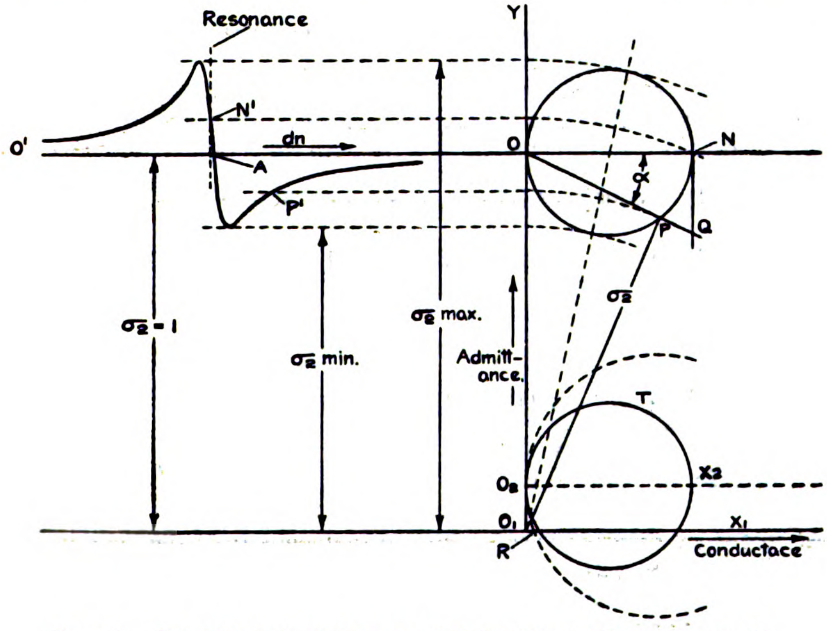


Fig. 22.—Graphical Solution for the Curves of Figs. 20 and 21.

Any point P' on the curve $O'N'P'$ of σ_2 has its corresponding point P on the circle ONP. Mallett has shown that the tangent of the angle $\alpha = PON$ is proportional to the frequency difference to which P corresponds from that to which N, the resonant frequency, corresponds.

(The circle is almost completely described for a frequency change of one part in a thousand.)

If we calculate the value of tan α in terms of σ_2 and $\sigma_{2\,\text{max.}}$ by simple trigonometry from Fig. 22 it will be found for the case where we have allowed σ_2 to be unity, as shown in Fig. 22, that tan α is given by the expression

$$1+\tan^2\alpha=\frac{\left(\sigma_{2\text{max.}}-\dfrac{1}{\sigma_{2\text{max.}}}\right)^2}{1+\sigma_2{}^2\pm\dfrac{2\sigma_{2\text{max.}}}{\sigma_2{}^2{}_{\text{max.}}-1}\sqrt{(\sigma_2{}^2{}_{\text{max.}}-\sigma_2{}^2)\left(\sigma_2{}^2-\dfrac{1}{\sigma_2{}^2{}_{\text{max.}}}\right)}}\quad . \quad . \quad (31)$$

an expression not containing "*dn*." For the case where C_1 is small and $\sigma_{2\text{max.}}$ is chosen equal to unity, the equation becomes

$$1+\tan^2\alpha=\frac{(1+\sigma_b{}^2)^2}{\sigma_b{}^2+\sigma_a{}^2\pm\dfrac{2\sigma_b}{1-\sigma_b{}^2}\sqrt{(1-\sigma_b{}^2)(\sigma_2{}^2-\sigma_b{}^4)}}\quad . \quad . \quad . \quad . \quad . \quad (32)$$

where σ_b stands for the base line value of σ_2 at frequencies removed from the immediate neighbourhood of response.

Referring back to the circle diagram of Fig. 22, the angle which the admittance vector *OP* makes with *ON* is, of course, the same which the corresponding reactance vector on the dotted reactance circle will make with the resistance axis O_2X_2. Hence, $\tan\alpha=\dfrac{1}{S_0K_0\omega}$, if q in equations (1) and (2) is put equal to $-\dfrac{K}{K_t}-\dfrac{2dn}{n}$. Inserting this value of q into (1) and (2) and calculating $S_0K_0\omega$ therefrom we obtain the very simple relationship

$$\tan\alpha=\frac{2dn}{n}\cdot\frac{1}{\varphi_2},$$

where *dn* is measured from the true response frequency.

On plotting tan α against "*dn*" a straight line should be obtained, the equation of which may be written $n=m\tan\alpha+n_0$, from which $\varphi_2=\dfrac{2m}{n}$, and n_0 is the true response frequency differing very slightly in frequency from the peak in Fig. 20 or from the point *O* in Fig. 21.

In an average satisfactory specimen of quartz this difference is not greater than one part in a hundred thousand. Examples illustrating the cases just considered are shown in Figs. 23 to 26.

The curves refer to the bar vibrating in its lowest longitudinal mode at a frequency of 44,000. The total air gap was 1 mm. Fig. 23 gives the experimental curve of σ_2, obtained for the case where C_1 is only the stray and parasitic earth capacities. The curve is drawn as a heavy line and the points observed are dots in circles.

From observations of "*n*" read off this curve at chosen values of σ_2, and from the calculated values of tan α, using equation (32), corresponding values of tan α and "*n*" have been plotted in Fig. 24. It will be seen that the points lie on a fairly good line, in view of the difficulty in accurately observing such small frequency differences from the curve.

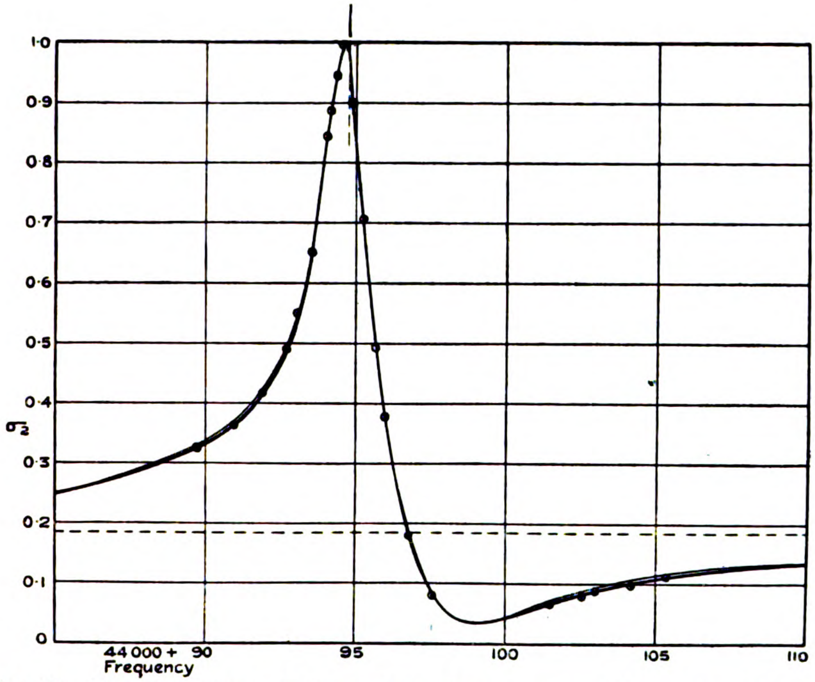


Fig. 23.—Experimental and Calculated Curves of the Type as in Fig. 20.

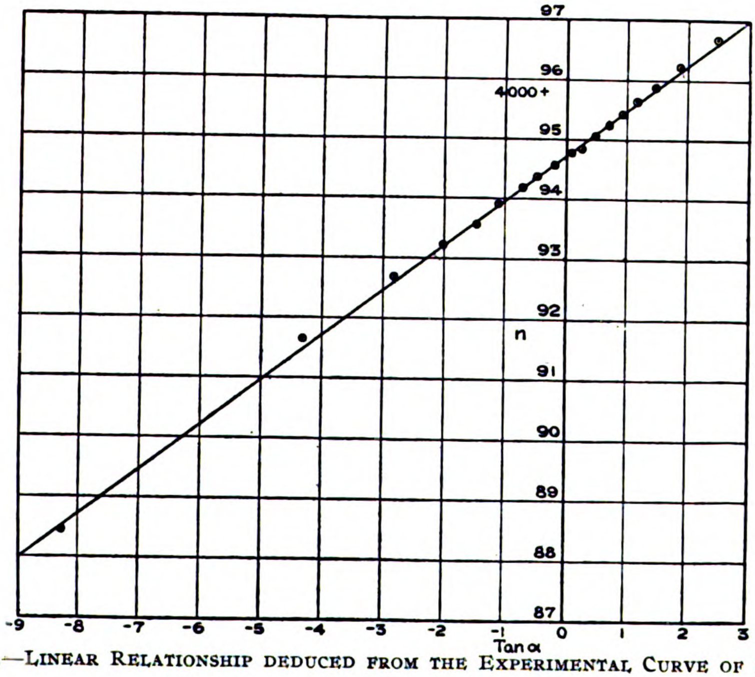


Fig. 24.—Linear Relationship deduced from the Experimental Curve of Fig. 23.

The slope of the line gives the value $34{\cdot}0\times10^{-6}$ for φ_2, which agrees very well with values obtained on other occasions by the other method. The response frequency occurs at $44{,}094{\cdot}7_2$, and is shown by a dotted vertical line on Fig. 23. From this value of φ_2, and from the known value of σ_b, the value of D has been calculated, using the equivalent equation to (29). The curve of σ_2 has then been calculated using equation (25) and multiplying the results by the factor necessary to bring $\sigma_{2\,\text{min.}}=$unity. The curve is shown as a fine line on Fig. 23. The agreement between the observed and the calculated curves is very good. Figs. 25 and 26 show the case of the same bar in the same gap, but the condenser C_1 has been made equal to $350\,\mu\mu$F. The line of Fig. 26 is fairly good, and the deduced value of $=33{\cdot}7\times10^{-6}$ is in very good agreement with the previous case. The agreement between observed and calculated curves in Fig. 25 is again remarkably good. It will be noticed that the frequency $n_0=44{,}094{\cdot}06$. There is a temperature coefficient of $+12\times10^{-6}$ in the tuning-fork multivibrator, in terms of which the frequencies were measured. The temperature difference of the fork for the two sets of measurements was probably 1°C. in the direction such that the second value 44,094·06 when corrected to the temperature of the first measurement becomes probably $44{,}094{\cdot}5_4$. The two

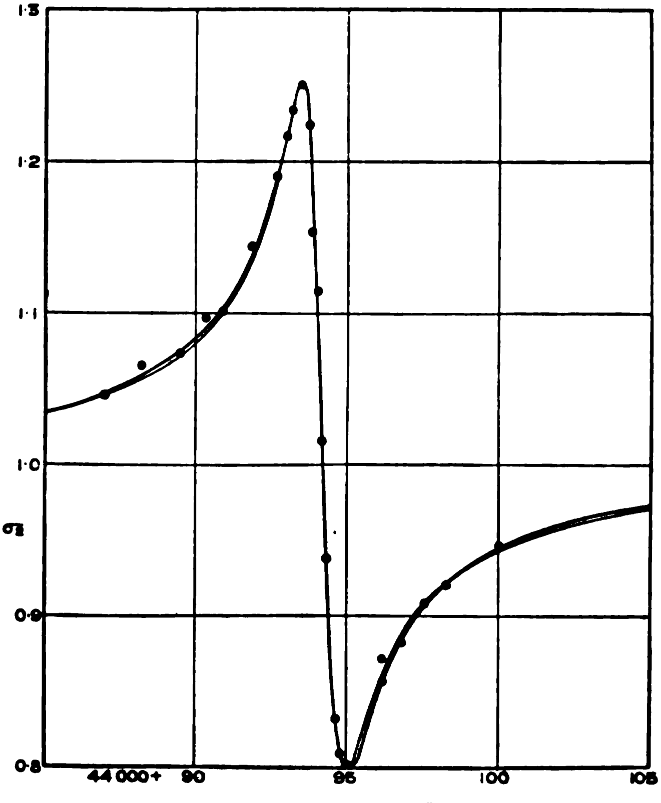


FIG. 25.—EXPERIMENTAL AND CALCULATED RESPONSE CURVES CORRESPONDING TO THE CASE OF FIG. 21.

frequencies differ, therefore, by only four parts in a million, which, in view of the fact that the two tests were made on different days, is a very satisfactory agreement.

The further analysis of the resonator by the use of various air gaps has not been carried out, but there is no reason to suppose that complete agreement with the results obtained by the other method would not be obtained. Curves similar to those of Figs. 23 and 25 have been obtained for other sizes of bar and for a plate vibrating transversely.

These experiments, therefore, uphold the equivalent network theory of the resonator, and are in complete accord with those made in the tuned circuit case.

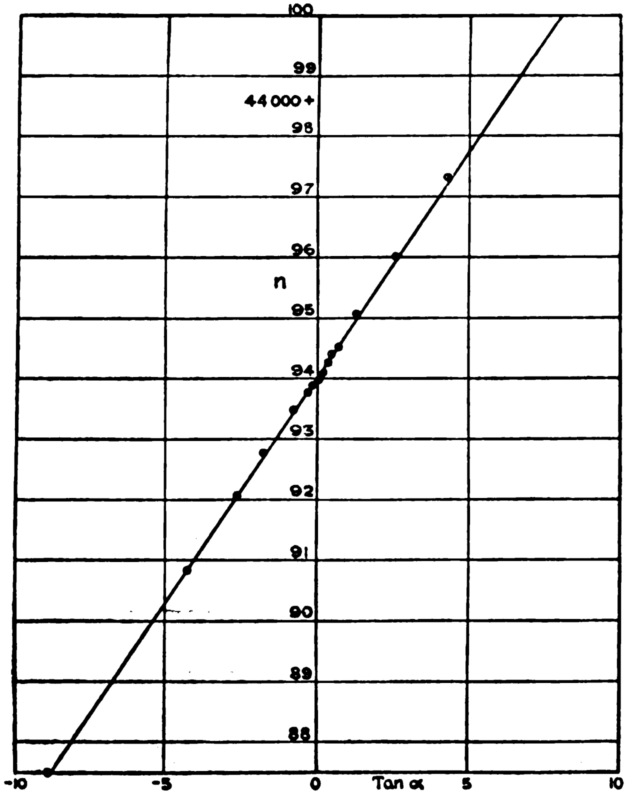


Fig. 26.—Linear Relationship deduced from the Experimental Curve of Fig. 25.

Before bringing this part of the Paper to a conclusion, the case (2) must briefly be considered, in which the current in the branch circuit containing the resonator is measured under the circuit conditions of Fig. 5, in which the resonator is shunted across an oscillatory circuit approximately tuned to the response frequency of the resonator.

If, from the original equations 1, 2, 3, we solve for I_2 in terms of the value to which it tends at frequencies near but outside the belt of response, we can express this as a ratio ρ_2 similar to what has already been considered as σ_2.

The general equation for ρ_2 becomes

$$\rho_2{}^2=\varphi_1{}^2\,\frac{\varphi_2{}^2+\left[q+\dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2}\right]^2}{\left[pq+\dfrac{pK(C+C_1+K_2)-q(C_1K_t+K_1K_2)-K(C_1+K_t)}{CK_t+C_1K_t+K_1K_2}-\varphi_1\varphi_2\right]^2+\left[q\varphi_1+p\varphi_2+\dfrac{\varphi_1K(C+C_1+K_2)-\varphi_2(C_1K_t+K_1K_2)}{CK_t+C_1K_t+K_1K_2}\right]^2}\ . \qquad (33)$$

where all the terms have exactly the same meanings as in previous equations. C_1 is a small parasitic capacity shunting the resonator itself, and includes the capacity of the electrodes outside the quartz, and of the leads to them. This capacity cannot be eliminated, and we cannot measure the true current flowing into the resonator itself.

In the original equation (4) for σ_1 we have not considered the effect of C_1. We are there dealing with the large current flowing through the inductance L. The effect of C_1 upon this is comparatively small, since C_1 is merely a small capacity in parallel with C.

If the full expression for σ_1 is worked out, including the C_1 term, it is found that, in order to express σ_1 in terms of the frequency difference from the bottom of the crevasse, it is necessary to substitute for q the quantity

$$q=-\frac{K(C+C_1+K_2)}{CK_t+C_1K_t+K_1K_2}-\frac{2dn}{n}$$

If this quantity is substituted into the equation for ρ_2 we get

Case I.—C=constant.

$$\underset{[C.\ \text{const.}]}{\rho_2{}^2}=\frac{A^2+(B-dn)^2}{\left[\dfrac{\varphi_2}{A\varphi_1}\ dn^2+dn\left(\dfrac{D}{B}+\dfrac{2\Delta n}{n\varphi_1}\right)-D+A)\right]^2+\left[dn(1+\varphi_2/\varphi_1)+A\left(\dfrac{D}{B}+\dfrac{2\Delta n}{n\varphi_1}\right)\right]^2}\quad .\ .\ .\ .\ .\ .\ . \qquad (34)$$

in which the following substitutions have been made :—

$$A=\frac{n\varphi_2}{2}\,;\quad B=\frac{nKCK_2{}^2}{2(C_1K_t+K_1K_2)(CK_t+C_1K_t+K_1K_2)}$$

$$D=\frac{nKCK_2{}^2}{2\varphi_1(CK_t+C_1K_t+K_1K_2)^2}$$

Note B and D have different meanings here from those used earlier in the Paper. In this equation C is constant, and may have any value whatever. The quantity "p" in such a case is best substituted by an expression of the form

$$p=-\frac{2\Delta n}{n}-\frac{2dn}{n},$$

where Δn is a constant frequency difference (generally small), depending upon the setting of C. It will be remembered that in equation (7*a*) for σ_1 it was noted that the equivalent term to $\frac{D}{B}+\frac{2\Delta n}{n\varphi_1}$ determined the asymmetry of the σ_1 curve.

Case II.—LC circuit adjusted so that at each value of dn, σ_1 is made a maximum

The case, in which C is varied in order that σ_1 may be a maximum, as in Cady's experiments, is complicated to work out accurately, because C appears in so many places in equation (5) for σ_1^2 when the quantity $(1-LC\omega^2)$ is substituted for p. But in many cases we may consider φ_1 and D constant as long as the changes in C are not more than a few per cent.

Under these conditions the only quantity which need be considered as variable, when C is varied, is the quantity "p."

The conditions for σ_1 to be a maximum with respect to variation of C are then reduced to a differentiation of the equation for σ_1^2 with respect to "p" as the variable.

Writing equation (5) in the form

$$\sigma_1^2=\frac{A^2+dn^2}{\left[-\frac{dn}{\varphi_1}p+\frac{D}{B}dn-(D+A)\right]^2+\left[\frac{A}{\varphi_1}p-dn-\frac{AD}{B}\right]^2} \quad . \quad . \quad (35)$$

and differentiating with respect to p it will be found that, for σ_1 to be a maximum, p must have the value

$$p=\frac{D\varphi_1}{B}-D\varphi_1\frac{dn}{A^2+dn^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The equations for σ_1 and ρ_2 become, by substitution of p as in (36),

$$\text{Max. } \sigma_1=\frac{A^2+dn^2}{AD+A^2+dn^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

$$\text{Max. } \rho_2^2=\frac{(A^2+dn^2)[A^2+(B-dn)^2]}{(AD+A^2+dn^2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Although we are strictly investigating ρ_2, and not σ_1 when σ_1 is a maximum, the equation for σ_1 is here given. It is seen to represent a symmetrical curve with respect to dn, and, unlike the previous equation for σ_1, equation (37) gives a curve rising asymptotically to unity and never falling again.

Equation (38) has been called $_{\text{max.}}\ \rho_2^2$. This is not strictly true when the variation of C is such as to make σ_1 a maximum when the fully accurate case is taken, because C appears in the numerator in the general equation for ρ_2 but is absent in that for σ_1. For all practical purposes, however, the term B in equation (38) may be considered independent of C so long as C is large compared with C_1 and K_1.

This equation represents the peculiar curve given experimentally by Cady. It is seen that when $dn=0$ a sharp minimum occurs on account of the bracket A^2+dn^2, also when $dn=+B$ another minimum occurs. Two maxima occur at values of dn near zero, one positive and the other negative (Fig. 27*b*).

It remains only to consider the changes in C necessary to satisfy the equation for p.

We may write for p the expression

$$-p=\frac{2dn}{n_0}+\frac{dc}{C_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where n_0 and C_0 are constant and are related by the equation $4\pi^2 n_0^2 LC_0=1$ and n_0 is the frequency at which $dn=0$.

If this value of p is substituted into equation (36) and, if also, we write $\frac{\Delta C}{C_0}=\frac{dc}{C_0}+\frac{D\varphi_1}{B}$ in order that capacity changes may be measured from the point $dn=0$, it will be found that

$$\frac{\Delta C}{C_0}=D\varphi_1\frac{dn}{A^2+dn^2}-\frac{2dn}{n_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

This equation gives the change in capacity necessary to make a maximum at each chosen value of "*dn*."

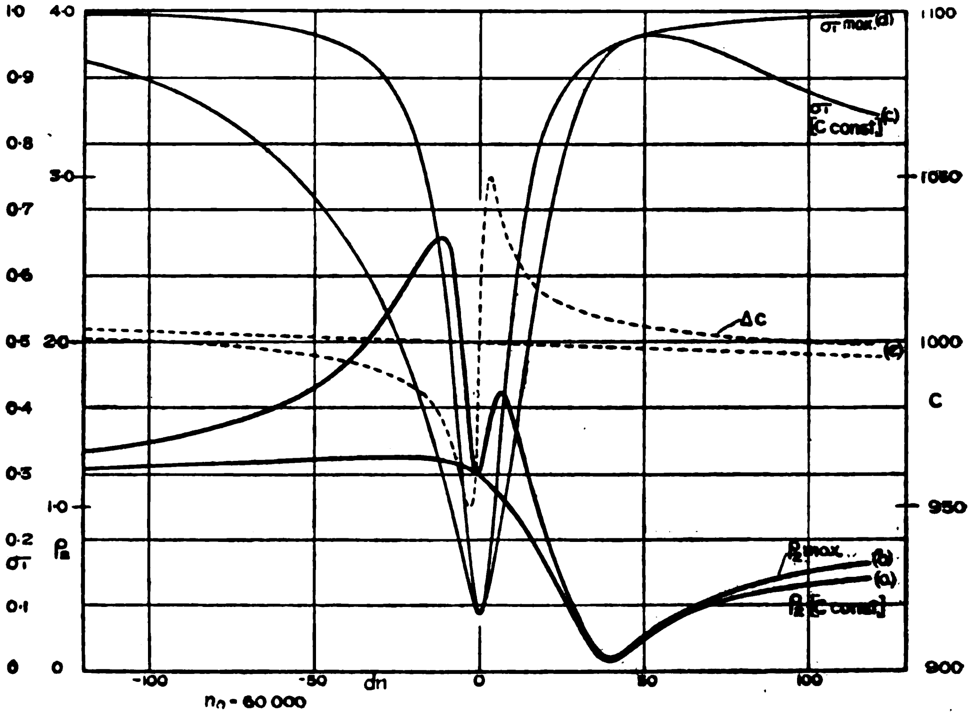


FIG. 27.—GROUP OF CURVES OF σ_1 AND ρ_2 FOR VARIOUS EXPERIMENTAL CONDITIONS OF THE CIRCUIT OF FIG. 5.

As examples of these equations, the set of curves shown in Fig. 27 have been calculated for the following assumed case :—

$$n_0=60{,}000, \quad A=\frac{n\varphi_2}{2}=3, \quad \varphi_2=100\times10^{-6}$$

$$D=30{\cdot}33, \ B=40, \ \varphi_1=1\times10^{-2}, \ \Delta n=-77{\cdot}5$$

The last term does not enter into the equations for $\sigma_{1\,\text{max.}}$ or $\rho_{2\,\text{max.}}$ but determines the asymmetry of σ_1. It has been given the arbitrary value of $-77{\cdot}5$ in order to make the curve for σ_1 reasonably but not too unsymmetrical.

The curves which have been drawn are as follows :—

(*a*) ρ_2 when C is constant (equation 33).
(*b*) ρ_2 when C is adjusted so that σ_1 is a maximum (equation 38).
(*c*) σ_1 when C is constant (equation 7*a*).
(*d*) $\sigma_{1\,\text{max.}}$ (equation 37).
(*e*) ΔC to satisfy equation (40) using a base line value of 1,000 $\mu\mu$F when $dn=0$.

The similarity of curve (*b*, *d* and *e*) to those observed by Cady will be noted and show that the simple algebraic method of considering the electrical system is substantially in agreement with observation.

A curve similar to (*a*) for a case where C was constant was observed, and gave a curve entirely in agreement in form with that calculated for the above fictitious case.

The equations given for $\varphi_{2\,\text{max.}}$ and $\sigma_{1\,\text{max.}}$ are only approximate when ΔC is, say, 10 to 20 per cent. of C_0, since all the terms containing C will be considerably changed. If, however, the alternative procedure of changing L were adopted, the equations would become exact and further deductions from them could be made in order to use this means of analysing the resonator mesh. The curve (*e*) would then, of course, be a curve of ΔL, and would be exactly the same in sense and proportions as that for ΔC.

In the example chosen the values of A, B and D are met by choosing the following reasonable electrical quantities :—

$$K_1=K_2=C_1=5\mu\mu\text{F}$$
$$K=0{\cdot}04\ \mu\mu\text{F and } C_0 \doteqdot 1{,}000\ \mu\mu\text{F}.$$

The large effect on ρ_2 of the parasitic capacity C_1 of 5 $\mu\mu$F is seen by consideration of B.

If C_1 is neglected

$$B \doteqdot \frac{nKK_2}{2K_1K_t} \doteqdot 120 \text{ cycles per second.}$$

Including C_1 at the assumed value of 5 $\mu\mu$F,

$$B \doteqdot 40 \text{ cycles per second.}$$

Since B represents the frequency difference between the two minimum values of $\rho_{2\,\text{max.}}$ and since also the value of $\rho_{2\,\text{max.}}$ at $dn=0$ is proportional to B, it is seen that the shape of the curve is very largely dependent upon C_1.

From the equations for $\rho_{2\,\text{max.}}$ a series of equations can be developed for the purpose of evaluating φ_2, K and K_1 when using such a method.

This φ_2 becomes given by the equation

$$\varphi_2=\frac{\delta n}{n}\sqrt{\frac{{}_{\text{max.}}\sigma_{1\ \text{min.}}\,(1-{}_{\text{max.}}\sigma_1)}{{}_{\text{max.}}\sigma_1-{}_{\text{max.}}\sigma_{1\ \text{min.}}}}$$

where δn is the frequency difference across the crevasse at a chosen value of $\sigma_{1\,\text{max.}}$ Other equations enable D to be obtained for various values of K_2 and φ_1, whereby K and K_1 are determined exactly as already developed.

II. EXPERIMENTAL.

A very great number of resonance curves have been made—two hundred or more—on resonators of all sizes from minute bars only 3 mm. long to bars 120 mm. long and 6 mm. thick; also on plates and discs from those only 0·2 mm. thick and a few mm. diameter up to a large block 20 mm. thick by 48 mm. by 30 mm. These have been examined not only with respect to their respective fundamental modes of longitudinal and transverse vibration, but also with respect to the overtone modes when the bar is vibrating in 1, 2, 3, etc., up to 9 or more segments. Except in certain very special cases, the electrical equivalent circuit has been found to hold true. The exceptions are those in which two response frequencies are so near together that the crevasses intersect one another.

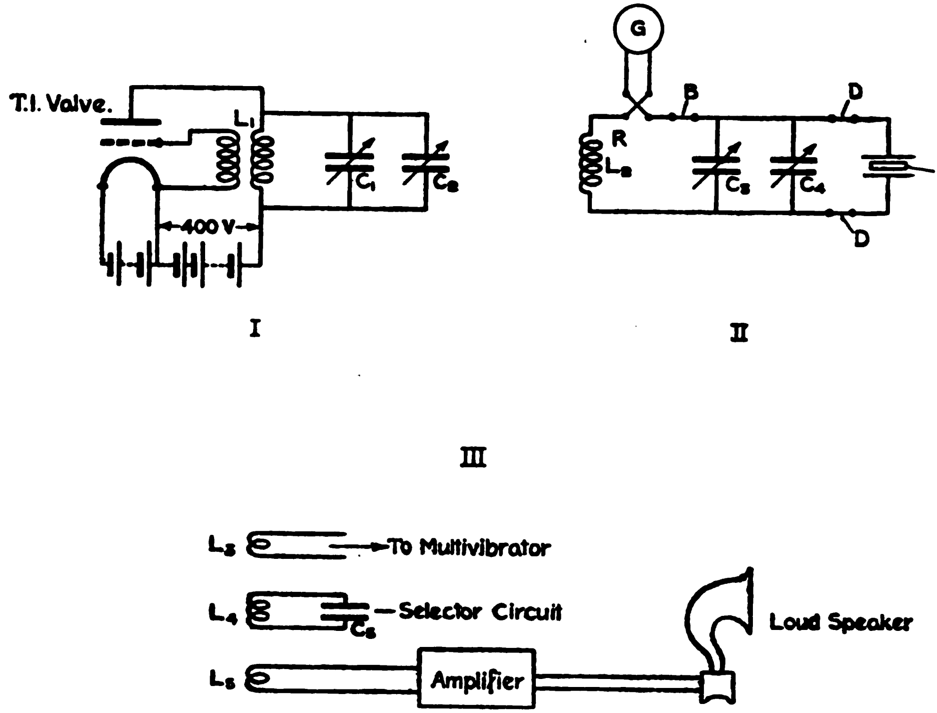


FIG. 28.—ARRANGEMENT OF APPARATUS USED IN THE MEASUREMENT OF σ_1 AND FREQUENCY.

Numerous measurements, referred to later, have been made on the temperature coefficient of response frequency and on other effects on frequency and damping not included in the theory.

A very great deal, however, remains to be done in several directions. The subject is one full of interest both from the scientific and practical points of view.

The following information and brief description of the experimental arrangements adopted may, therefore, be of interest.

Measurement of σ_1 *and of Frequency.*

The apparatus was arranged as in Fig. 28, and consists of three parts:—

(i) The source, in the form of a simple valve oscillator of ordinary type, and not of the type in which the frequency is controlled by a master valve feeding the grid of a power valve.

It consists of a 250 watt valve, excited from a 400 volt accumulator battery. The inductance and grid coils L_1 are constructed to keep constant in inductance and that coil in the oscillatory circuit is of small log. dec. These qualities are important where it is necessary to reduce the drift of frequency with time to the smallest amount.

The main part of the oscillatory circuit capacity C_1 was in the form of mica condensers of the clamped type. These again are very invariable in capacity with respect to temperature. In general, C_1 was at least 15,000 $\mu\mu$F. C_2 consisted of two variable standard air condensers in parallel, one had a range of about 1,500 $\mu\mu$F and the other was of a much smaller range with an open scale on which a change of 0·1 $\mu\mu$F was easily observed. Sometimes the open range condenser was connected across only a few turns of the inductance coil in order to secure greater openness of the frequency scale. All the condensers were screened in metal cases connected together and to earth. The variable condensers were fitted with long handles to enable precise adjustments to be made from the position at which the galvanometer scale was located.

(ii) The test circuit consisted, in general, of the oscillatory circuit formed by a standard inductance coil L_2 and screened variable air condenser C_3, usually shunted by an open scale small condenser C_4. A vacuum thermo-junction and heater current measurer was inserted where shown and connected to a bifilar galvanometer of good zero-keeping qualities.

A small mercury contact link at *B* served as a switch and as a gap for the insertion of known standard high-frequency resistance units when so desired.

The quartz resonator mounted in its special gap was connected by thin wires via mercury links *DD* to the terminals of the condenser C_3. In many cases the resonator was left open to the room, but in others, and particularly in the temperature coefficient measurements, the resonator was placed in a simple electric oven thermostatically controlled in temperature at any desired value up to 50° C. Arrangements were also made to pump dry air into the oven on occasion in order to ensure that moisture did not condense on the quartz on cooling.

The observations made were those of σ_1 at various settings of the Condenser C_2 in the source. The preliminary settings on C_3 and C_4 were first made so that the conditions desired in the test circuit were obtained such as $LC_4\omega^2=1$ when $dn=0$, etc. The coupling was adjusted so that 100 σ_1 on each side of the crevasse was about 99·8 in a normal case, as this was the value found by experience and by calculation to represent the condition $\sigma_0=1{\cdot}000$ in the absence of the resonator.

The adjustments of the condensers C_1 and C_2 were such that C_2 was at about the middle of its scale when σ_1 was at $\sigma_{1\,\mathrm{min.}}$ Readings of σ_1 were then taken at various settings of C_2 suited to the accurate delineation of the curve.

Frequency Measurements.

The arrangements for the measurement of the frequency of $\sigma_{1\,\mathrm{min.}}$ and of the frequency changes corresponding to changes in C_2 were made with very great accuracy by the help of the standard multivibrator wavemeter of the Laboratory.

These arrangements are merely outlined in Fig. 27 as (iii), and the reader is referred to the author's original Paper(6) for information regarding the wavemeter itself. It will suffice to say that impulses of exactly known frequency are sent through a coil L_3 which is loosely coupled to a resonant circuit L_4C_5 of small damping coefficient. The condenser of this circuit is variable and is calibrated in terms of harmonics of the frequency of the impulse current through L_3. By setting the condenser C_5 to the reading corresponding to a chosen harmonic, this frequency is reinforced and interferes with that of the source (i). The two frequencies are received by a selective amplifier tuned to resonance, and after rectification and amplification the telephonic frequency beat note is heard in the loud-speaker.

The multivibrator source is controlled by a valve-maintained tuning-fork. The tuning-fork frequency is so constant that it confers upon the whole system of frequency measurement a most remarkable and unique property which is worthy of mention.

We have, in the wavemeter, the following system. A valve-maintained tuning-fork of frequency adjusted to 1,000·00 cycles per second. This fork, of elinvar steel, has a temperature coefficient of frequency of +12 parts in a million per 1°C. rise in temperature.

This tuning-fork controls a low-frequency multivibrator of 1,000 impulses per second.

All harmonics up to the one hundred and twentieth can be selected from this multivibrator so that a " spectrum " of frequencies up to this limit is obtained by simple selection on the harmonic-selector circuit.

Higher frequencies are obtained by the use of a second multivibrator giving impulses at the rate of 20,000 per second. This multivibrator is kept in harmonic synchronism with the low-frequency one by the intermediary of a fixed-frequency resonant circuit set to 20,000 cycles per second, and a single-valve amplifier.

By the help of additional coils on the selector circuit, harmonics up to about the seventy-fifth can be selected from this multivibrator.

It will be seen therefore that the source can be directly set to any frequency that is an integral number of kilocycles per second up to 120 kc/s by the aid of one multivibrator and to any frequency which is an integral multiple of 20 kc/s up to about 1,500 kc/s. Actually, however, all the intermediate integral kilocycles per second can be successively set and counted round between any two main harmonics such as the thirtieth and the thirty-first on the high-frequency multivibrator giving 600 and 620 kc/s respectively.

Not only can such frequencies be exactly set on the source, but a very great many other subsidiary frequencies may be obtained within the belt of a thousand cycles per second.

Thus, whenever the source has a frequency very close to that represented by the formula

$$n=1{,}000\left(f\pm\frac{1}{r}\right),$$

where f and r are integers, a slow-synchronization beat is heard. For example, in the case of the resonator of 44,000 cycles per second the following frequencies may be exactly set on the source without any auxiliary apparatus: 44,100, 44,111·1, 44,125, 44,142·8, 44,166·7, etc. With care, further intermediary frequencies can be located between these, such as

$$44{,}125+\frac{142{\cdot}8-125}{1,\ 2,\ 3,\ \text{etc.}}$$

This property of the tuning-fork-controlled multivibrator is quite unique and is only possible on account of the extreme steadiness of frequency of the tuning-fork.

The following table gives a typical set of observations as actually taken on a resonator and shows that it is never necessary to interpolate by more than about two cycles per second from a frequency that is known:—

TABLE III.

Condenser Reading.	Partial Harmonic.	Frequency, 44,000 +	$100\sigma_1$
50			98·4
53·2	$\frac{1}{9}$	111·1	98·0
60			97·7
65			96·7
70			95·6
75			93·75
78·0	$\frac{1}{9·333}$	107·2	90·9
81			88·4
84			85·2
87			80·2
89·6	$\frac{1}{9·5}$	$105·2_5$	73·2
92			65·7
95			56·6
97			44·4
98			34·6
99			$33·2_5$
100			$33·2_5$
101			34·55
99·5			33·05
102·8	$\frac{1}{9·667}$	103·4	36·4
103			40·8
104			44·6
106			58·8
107·6	$\frac{1}{9·75}$	102·5	58·8
110			67·2
114			77·2
120			86·3
123·5	$\frac{1}{10}$	100·0	89·4
130			93·0
135			94·8
140	$\frac{1}{10·25}$	97·6	96·6
—	$\frac{1}{10·5}$	95·2.	97·7
—	$\frac{1}{11·0}$	90·9	99·1

The frequencies corresponding to the partial harmonics such as $\frac{1,000}{9·5}=105·2_5$, etc., have been inserted in the table as accurately known frequencies self-determined by the wavemeter. The other frequencies are obtained by interpolation from a line drawn through these known frequencies when plotted against condenser reading.

It will be seen from the figures that the uncertainties associated with the frequency corresponding to any observed value of C_2 are only of the order 0·1 cycle per second at any part of the curve.

Observations of σ_2.

These were made using a Duddell thermo-galvanometer in which the heater was a thin platinized-quartz rod. The resistance was about 120 ohms and the sensitivity such that full-scale deflection was obtained with a current of about 0·5 milliampere.

In these observations we are dealing with a circuit that is not in resonance, but which is almost a pure capacity. As a consequence the voltage which must be induced is much greater than when a resonant test circuit is used. Closer coupling to the source is therefore necessary for a given energy dissipation in such a case. The changes in frequency are confined to such a narrow belt when observing curves such as those of Figs. 24 and 25 that reaction on the frequency of the source may become troublesome. It is for this reason that it is considered highly desirable to use the resonant-circuit method of determining resonant frequency. A disadvantage of the method whereby the constants of any electrical circuit at radio frequencies are determined by the change in effective reactance rather than in effective resistance is that it becomes almost essential to use a source complicated by the addition of a master-valve oscillator to keep the frequency in the power-valve generator independent of load.

It might be argued that the point of response frequency is defined much more sharply in a curve of the type in Fig. 25 than in one of the crevasse type owing to the fact that one curve runs through the response frequency at a steep angle, whilst the other is the less-well-defined horizontal tangent. In some systems not highly resonant this is true and for such systems the measurement of resonant frequency is best made by the more accurate method. In the case of a quartz resonator the trouble is, not to determine the resonant frequency, but to avoid missing it altogether owing to its extreme sharpness of location. The accuracy of location is extraordinarily great by the method using a resonant circuit. The variations possible in the response frequency due to other causes in the mounted resonator are far greater than any uncertainty due to the method of observation.

Although in the experiments here described the frequencies have been measured with an elaborate and very accurate standard, it is not at all essential to use such a method for the purpose of investigating the equivalent electrical properties of resonators. With the exception of measurements of temperature coefficient and effects which require a considerable time in their determination, the changes in frequency may be observed by simple calibration of the changes in the source when C_2 is varied, using an auxiliary oscillator of frequency which is sensibly constant during the experiments. A second similar quartz oscillator could also be used, of course.

The *temperature* coefficients of frequency of resonators will now be discussed.

Temperature Coefficients of Frequency.

The temperature coefficient of any standard is frequently of vital importance, and in view of the precision obtainable in other respects the variations with temperature of the response frequency of resonators should be known.

Measurements of this quantity were therefore made on a considerable number of resonators and on three oscillators.

Considerable trouble was experienced at first in the measurements owing to the concurrent variations in the air gap with temperature masking the true changes in the response frequency.

These were overcome by the use of suitable mountings for the electrodes, and the careful adjustment of the resonator between them.

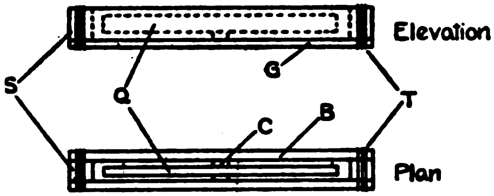


FIG. 29.—HOLDER FOR A LONGITUDINAL RESONATOR FOR TEMP. COEFFICIENT OF FREQUENCY MEASUREMENTS.

For the longitudinal resonators the form of electrodes and the mounting of the resonator were as shown in plan and elevation in Fig. 29.

The electrodes are the narrow brass plates *B* having their inner faces smooth and flat. These are kept at an accurately known and constant distance apart by small distance pieces of fused silica *S*, having plane parallel faces. The base consists of a narrow glass slip *G*, having a small piece of cork *C* stuck on transversely at the centre of its upper surface. The electrodes with their separators and the glass slip are bound together at each end by silk thread. A narrow trough is thus formed within which the resonator is centrally balanced on the narrow cork support. Using this form of mounting remarkably consistent results could be obtained notwithstanding the fact that in some cases the temperature coefficient was only 2 or 3 parts in a million per 1°C.

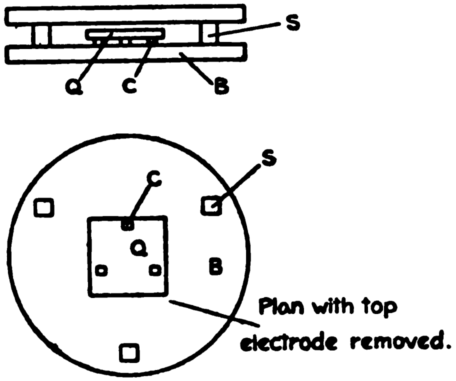


FIG. 30.—SAME AS FIG. 29, BUT FOR A TRANSVERSE RESONATOR.

The arrangement for the transverse resonators was the same in principle as that described above, but disc or rectangular shaped electrodes were used. The lower electrode as shown in Fig. 30 was horizontal. Upon this the resonator was rested on three minute pieces of cork sandpapered to the correct thickness. Three pieces of fused silica of equal thickness with parallel faces served to support the upper electrode.

The mounted specimens were placed in a simple temperature controlled oven, and the response frequencies were measured over a range of temperatures from about 12°C. to about 40°C. Much higher temperatures could have been explored if desired, but for the purpose in view the range given was considered sufficient.

Several longitudinal resonators of various lengths and shapes were measured, and three or four transverse resonators were also observed.

In the use of some of the longitudinal resonators various overtone modes of vibration were measured, since these gave results of considerable interest.

Some complete mounted resonators as made by Messrs. Hilger were also tested, and the author is indebted to them for permission to include these results.

The bars measured had the dimensions as given in the table below :—

TABLE IV.—*Longitudinal Resonators.*

Length in millimetres.

Designation.	Length.	Thickness.	Breadth (along optic axis)
A	47·0	3·3	7·50
B	62·2	1·52	7·54
C	62·5	1·49	7·50
D	9·86	6·72	7·54
E	Hilger Resonators—	Dimensions unknown.	
F	..	..	
	Transverse	*Resonators.*	
G	19·18	2·71	14·61
H	16·42	6·15	14·65
I (disc)	36 mm. diam., 6mm.	thick.	

The results obtained on these bars were as follows :—

TABLE V.

Bar.	Mode of Vibration.	Frequency, cycles per second.	Temp. coeff. parts in a million.	φ_2
A	Fundamental	58,675	$-1{\cdot}0_3$	75×10^{-6}
	Overtone in 3 segments	174,450	$-3{\cdot}0_6$	...
	,, ,, 5 ,,	273,750	-49	...
	,, ,, 7 ,,	414,000	-70	...
B	Fundamental	44,120	$-4{\cdot}0_0$	27×10^{-6}
	Overtone in 3 segments	130,850	$-15{\cdot}0_3$	55×10^{-6}
	,, ,, 5 ,,	219,840	$-5{\cdot}0_2$	$19{\cdot}5 \times 10^{-6}$
	,, ,, 7 ,,	304,650	-66	22×10^{-6}
C	Fundamental	43,517	$-3{\cdot}0_1$	70×10^{-6}
D	Fundamental longitudinal	413,600	-27	60×10^{-6}
	Fundamental in axis direction	385,260	-51	35×10^{-6}
	Fundamental in axis direction after grinding twined portion away	337,750	-80	47×10^{-6}
E	A. Hilger complete resonators	123,031	Less than 0·2	...
F	,, ,, ,,	470,800	-16	45×10^{-6}

TABLE VI.—*Transverse Resonators also Usable as Oscillators.*

Bar.	Mode of Vibration.	Frequency, cycles per second.	Temp. coeff. parts in a million.	φ_2
G	Fundamental transverse	847,050	−53	53×10^{-6}
H	,, ,, ...	472,150	−34	22×10^{-6}
I (disc)	Complete mounted crystal in disc form, fundamental transverse	455,500	−26	43×10^{-6}
	Fundamental longitudinal	75,300	−40	47×10^{-6}
	,, ,, in direction of optic axis	106,230	−74	40×10^{-6}

These results are of great interest, but can only be considered fragmentary. Much valuable information would be gained by a complete investigation of the temperature coefficients with special reference to the proportions of length, width and thickness of the bar or plate and with respect to various air gaps.

The ratios of the various frequencies could doubtless be made to yield information regarding the mode of vibration when considered in conjunction with the mathematical theory of resonance in bars or plates. These considerations require a complete investigation in themselves and lie outside the scope of the present Paper.

Returning to the temperature coefficients of frequency it is seen that for the fundamental mode and for the overtone modes in three segments the coefficients are very small.

The coefficients in the direction of the electric axis (transverse mode of vibration) and in the direction of the optic axis (as in disc I) are very much larger.

Measurements of the coefficients of linear expansion and of Young's modulus have been made by various experimenters, and extracts from their results are quoted in a recent Paper by Bragg(4) on the crystal structure of quartz.

I am not at the moment aware that the coefficients of Young's modulus in a transverse plane of the crystal and specifically along and perpendicular to the electric axis under conditions of pure tensile stress in these respective directions have been made, but it would appear that the differences are very great, and that the coefficient of Young's modulus in directions perpendicular to the electric and to the optic axes is smaller than was hitherto supposed.

The method of frequency change is, at any rate, a specially suitable one for the purpose of carrying out such measurements.

The larger coefficients for the higher overtone modes of vibration occur, I think, as a result of the shortness of the vibrating segment. With a segment of length of the same order as the width of the bar the modulus along the crystal axis will exert an influence on the mode of vibration and on the frequency, so that the stresses are no longer even approximately pure, such as will be the case for the fundamental mode of longitudinal vibration of a thin rod, in which a transverse plane section will vibrate with a nearly pure translational motion.

In those cases in which it was observed the value of φ_2 is included in the Table for the various resonators in their various modes of vibration. It will be seen that this quantity varies irregularly with the mode of vibration in the same bar, due, no doubt, to the non-uniformity of the quartz. It is practically impossible to obtain a specimen bar 6 cms. long which is entirely free from visible twinning when examined under the polariscope. If a mixed portion of the bar comes at a node for a particular mode of vibration it is certain to cause a diminution in amplitude and an increase in the log. dec. of the vibrations. It may be that the anomalous temperature effects in Bar B are associated with the variations in φ_2.

Three conclusions which may be drawn from these measurements of temperature coefficient are :—

(1) That the temperature coefficient of response frequency for a thin bar when vibrating longitudinally is small and in a good specimen is of the order -5×10^{-6} per 1°C. rise in temperature.

(2) The temperature coefficient of response frequency of a disc or plate vibrating transversely in the direction of the electric axis is of the order -40×10^{-6} per 1°C. rise in temperature and is, therefore, by no means negligible. Values ranging from -30 to -70×10^{-6} have been observed.

(3) The temperature coefficient of response frequency of vibration in the direction of the optic axis is larger than either of the foregoing and may reach -80×10^{-6} per 1°C. rise. Also in the case of a disc or plate in which the dimensions along the optic axis and along that axis which is perpendicular to it and to the electric axis, the temperature coefficients of all the modes of vibration are large.

A number of properties of resonators not embraced by the foregoing theory, but nevertheless of importance for design, were investigated and may be summarized shortly in conclusion.

I. EFFECT ON RESPONSE FREQUENCY OF DISPLACEMENT OF THE RESONATOR FROM ITS POSITION OF CENTRALITY IN A FIXED AIR GAP.

Observations were made of the change in response frequency when a resonator was displaced transversely by successive amounts from the position of centrality within the gap to the position in which one face of the resonator was practically in contact with the electrode. The resonator experimented upon was a bar 62 mm. long, 7·5 mm. deep, and 3·3 mm. thick, the last-named dimension is in the direction of the electric axis.

The observations were only made upon the fundamental longitudinal mode of vibration which had a frequency of about 43·8 kilocycles per second.

The results for two different air gaps are given in the following Table :—

TABLE VII.

Displacement of Bar, mm.	Frequency Change Parts in 10^6	
	Total Gap 0·7 mm.	Total Gap 2·7 mm.
0	0	0
0·1	−8	−2
0·2	−32	−8
0·3	−80	−18
0·5	...	−44
0·7	...	−78
1·0	...	−153
1·35	...	−284

According to theory, there should, of course, be no change in response frequency whenever the bar is within the gap since the capacity K_2 consists of two condensers

K_a, K_b in series, where a and b are suffixes to identify these capacities with air gaps a and b on either side of the resonator,

$$K_2=\frac{K_aK_b}{K_a+K_b},\quad \text{but } K_a=\frac{B}{A} \text{ and } K_b=\frac{B}{b}$$

where B is a constant.

Hence
$$K_2=\frac{B_2/ab}{B/a+B/b}=B/(a+b)=\text{const.}$$

The displacement of the resonator does not alter $a+b$ and hence K_2 does not change. We have already seen, however, by the curve of frequency change (Fig. 16) that the actual change in response frequency is greater than that predicted by theory and that this is probably due to a change in K consequent upon the reaction of the self-induced electric field upon the effective permittivity of the quartz.

It is to be expected, therefore, that the asymmetry of this induced field resulting from the displacement of the resonator will have the effect observed.

Whether the above explanation is correct or whether the cause of the effect is that the electric flux due to the applied field does not remain constant when the resonator is asymmetrical requires further examination. It is, however, quite clear that the effect is by no means negligible from the standpoint of the use of such resonators as frequency standards.

The bar here quoted as an example is relatively thick; in practice the use of a thickness of 3 mm. on a bar 60 mm. long would be considered rather extravagant. With such a bar a possible variation of response frequency of one part in ten thousand can occur if it is mounted with a total gap of 0·7 mm. and no precautions are taken to locate it within the gap. In practice it would be more probable that a thickness of 1·5 mm. would be used for the bar. In such a case a similar frequency range would occur if the total gap were only 0·3 mm. With a smaller gap the total range of frequency due to displacement will be smaller, but on the other hand, the rate of change of frequency is greater. In the case of a bar 1·5 mm. wide with a total air gap of 0·3 mm. the rate of change of frequency with change of air gap would be about +4 parts in a hundred thousand for an increase in air gap of 0·01 mm. A reduction of the air gap to 0·2 mm. would reduce the changes due to asymmetry, but would increase those due to a possible change of 0·01 mm. in the actual gap.

As in so many other cases, the best design is a compromise between conflicting conditions and depends chiefly upon the permissible cost in materials and construction.

Experiments on Oscillators.

Although this Paper deals mainly with the analysis of piezo-electric crystals as resonators because such analysis can be more easily undertaken on resonators than on oscillators a considerable amount of experience has been gained with respect to the behaviour of crystals mounted and used in conjunction with a triode in such a manner as to be self-maintaining. The advantages of such a method of use need no elaboration, their use in such a manner has been described by Cady, Pierce and other experimenters.

With regard to the effects of variation of air gap upon the frequency of maintenance of oscillators a number of experiments made by the author have shown that the changes are exactly parallel with those obtained on the same specimen when tested as a resonator.

Similarly also with regard to temperature coefficient: this has been found to be the same whether the crystal is tested as an oscillator or as a resonator.

There seems no reason to doubt, therefore, that a similar equivalent electrical network will account for the behaviour of the crystal when functioning as an oscillator as when used as a resonator.

The response frequency as a resonator and the frequency of the self-maintained vibrations as an oscillator are, however, considerably different; in the latter case the frequency is higher so that the crystal considered as a two-terminal piece of apparatus is behaving as a large positive impedance at the self-maintaining frequency. A complete mathematical treatment of the mounted crystal when attached to a valve system is necessary before the significance of this fact can be appreciated. This is not attempted in the present Paper, but the changes in frequency of an oscillator consequent upon the addition of a small capacity across the grid filament circuit suggest that the internal valve capacities are an essential factor in the maintenance of the oscillations and that the grid filament effective input capacity is responsible for the observed frequency difference between resonator and oscillator.

The conditions of operation are, however, more severe for an oscillator. The quartz itself has to be chosen with particular care. In general, a better specimen must be chosen for an oscillator than for a resonator. It must be ground with more care and the faces must be left of a finer matt surface without noticeable scratches. The air gaps have of necessity to be much smaller in order that sufficient reaction on the valve may be obtained to enable it to supply the necessary energy for maintenance of the oscillation. In one simple arrangement the crystal is in the form of a disc or rectangular plate and rests by its own weight on the lower electrode whilst the upper electrode is either lightly pressed upon the upper surface or is otherwise supported, leaving a very small air gap. Observations have shown that considerable variations of frequency are possible—of the order of one part in ten thousand—depending upon the exact condition of the crystal. There appears to be a settling-down or movement into closer apposition with the lower electrode resulting in a slow drift in frequency with time and an increase in the log. dec. of the oscillator so that it is maintained less vigorously in vibration under fixed external conditions. The normal behaviour is usually restored upon turning the mounted crystal upside down and replacing it or by tapping it; it seems necessary that it should " float " on a certain minimum thickness of air in order to operate satisfactorily. I have found that the use of three minute supports for the crystal leaving an air gap of 0·1 mm. results in a satisfactory behaviour.

Considerable difficulties arise in the construction of oscillators for frequencies higher than 3×10^6 cycles per second. The thickness must be uniform to about 0·001 mm. and the proportions of width and length to thickness appear to be of considerable importance. Further investigation on the technical aspect of the production of satisfactory high-frequency oscillators is necessary.

Conclusion and Comments.

1. The conclusions to be drawn from the experiments and simple theory given here would appear to be that an electrical network of the kind first suggested by Butterworth can explain in a general way the behaviour of a piezo-electric resonator

or oscillator. It may be mentioned in passing that before finally using Butterworth's system the writer had developed the system given in Fig. 31 and had found that this system gave a satisfactory explanation of the resonator. It is, in fact, interpretable almost exactly algebraically into the system of Fig. 2. The system actually adopted is, however, somewhat more convenient to use and satisfies the imagination as corresponding more nearly to the physical truth.

With regard to the analysis of the resonator in order to find K, K_1 and S, a matter of considerable theoretical interest, which has purposely been omitted until now, must be mentioned.

An inspection of the equivalent electrical circuit of the resonator shows that at frequencies outside the region where $NK\omega^2$ is nearly unity, the resonator should revert to a simple series circuit consisting of K_1 and K_2 in series, K_2 being the air-gap capacity and K_1 the quartz capacity, calculable from its dimensions and known dielectric constant. It can, of course, be measured also by a direct replacement method at frequencies on each side of the response frequency.

In the case of the longitudinal resonator the calculations and the measurements were made. The value found for K_1 was $11{\cdot}0_7\mu\mu$F, whereas the value at resonance deduced from the crevasses was found to be $8{\cdot}0_7\mu\mu$F. It seems clear, therefore, the effective value of K_1 at resonance is definitely smaller than the geometrical value, as a result of the self-induced electric field. These measurements are difficult, and the probable error in the experimental determinations in the two cases is certainly not less than $0{\cdot}3\mu\mu$F. It is believed, however, that this difference is real. It is interesting to recall in this connexion that in the note in the Phys. Rev. (7) the statement is definitely made there (*see* Ref.(7)) that K_1 at resonance is given by an expression of the form

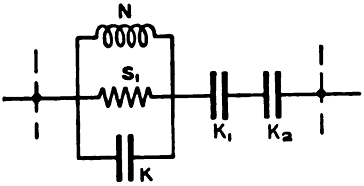


FIG. 31.—ALTERNATIVE EQUIVALENT NETWORK FOR A RESONATOR.

$$K_1=\left(\frac{K}{4\pi}-\delta\varepsilon\right)\frac{bl}{e}$$

where $\frac{Kbl}{4\pi e}=K_1'$ is the geometric capacity and $\delta\varepsilon\frac{bl}{e}$ is a capacity resulting from the reaction of the electric field upon K.

It is interesting to find that the difference observed is in the direction predicted by the theory of Van Dyke, but the amount found in the experiments described here is much greater than the 1 per cent. found for a resonator of Cady's.

It is probable that the term $\delta\varepsilon$, which is given for the case in which the electrodes are in contact with the quartz, will be multiplied by a considerable factor when there is an air gap, since under these latter conditions the voltage gradient in the quartz is enormously increased.

Thus we have seen, from equation (*a*) and Fig. 4, that the resonator behaves at the response frequency almost exactly as a non-inductive resistance of value $S\,\frac{K_t^2}{K_2^2}$ by substitution of $-\frac{K}{K_t}$ for q. In a case where $K_1=K_2$ the effective resistance becomes $4S$.

The r.m.s. current I_3 taken by the resonator will be $E_2/4S$, where E_2 is the r.m.s. voltage applied to the terminals. But the voltage across K_2 will be given by $I_3/K_2\omega$; hence the ratio of these voltages is, in the case taken, equal to

$$\frac{1}{4SK_2\omega}=\frac{1}{\varphi_2}\,\frac{K}{4K_2}$$

Assuming normal values of 0·001 for $K/4K_2$, and 30×10^{-6} for φ_2, the ratio of voltages becomes 30. The average r.m.s. voltage across the air gaps is therefore about 30 times that applied to the electrodes. This fact has been used in a beautiful manner by Giebe by placing the mounted resonator in a vacuum so that a visible glow occurs in the air space when the response occurs. The mean r.m.s. voltage across the quartz will therefore also be about 30 times the applied voltage. The gradient over the middle portion of the bar will be considerably greater than that towards the ends.

The voltage gradient is a maximum at the centre of the bar, and has approximately a sine wave distribution from the centre to the ends.

In the case of the transverse resonator completely analysed, the similar measurements at frequencies on each side of the response frequency were made. In this case, however, the statical capacity found for K_1 was $1{\cdot}6\mu\mu$F, whereas the vibrational capacity found was $1{\cdot}9_3\mu\mu$F, so that the difference here is reversed in sign. Cady does not state whether the vibrational capacity K_1 should be greater or less than the statical K_1' for a resonator vibrating transversely in the form of a plate under the longitudinal piezo-electric effect. The measurements in the case of the small transverse resonator here investigated are, however, even more uncertain than those on the longitudinal resonator, owing to its shape. No great weight can therefore be attached to this difference.

With regard to the calculation of K_1' and K_2, also from the area of the quartz and from the air gap, it may be objected that it is not justifiable to do this using the simple formula on the assumption of an undisturbed electric field. It is realised that to a considerable extent this is true, but at the smaller air gaps the effect will be very small, and at the larger air gaps K_2 has a value which is small compared with K_1', and does not exert much influence on the behaviour. In any case, the straightness of the lines deduced from observations of $\sigma_{1\,\mathrm{min.}}$ with various air gaps and with various values of φ_1, is undoubted, so that the question of an error in K_2 then really resolves itself into a question of units—viz., that K, K_1 and K_2 are all in the same units, but that these may not be strictly $\mu\mu$F units, but that the units are such that by calculating from the simple capacity formula the behaviour of the resonator is consistently explained when used on an external circuit in which the units of capacity is the $\mu\mu$F.

Further work is needed on resonators of larger capacity in order to elucidate the departures of the behaviour of the resonator from the predictions of the theory, in particular in respect of K_1, which is definitely different from its value at frequencies outside the belt of response owing to the self-induced electric field. In this respect it is probable that as found at the point of maximum response, K_1 really increases from this value to nearly its geometric value as the value of σ_1 rises to unity on each side of the crevasse.

This change cannot easily be elucidated from the curves of σ_1 or σ_2, since K_1 is of comparatively small influence on the shape of these curves.

The reaction of the self-induced electric field on K acting as a cause of departure of the response frequency change from that given by theory will also repay further investigation.

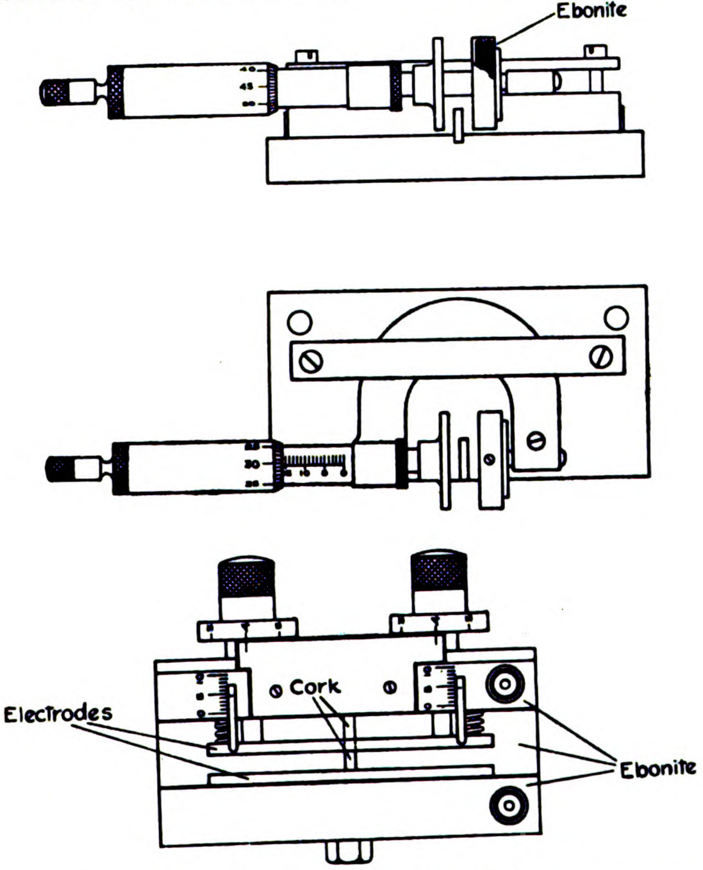


FIG. 32.—ADJUSTABLE AIR GAPS FOR OBSERVATIONS ON RESONATORS WITH VARIOUS VALUES OF K_2.

In connexion with such more complete investigations, the use of a separate small variable air condenser in series with the resonator has not been overlooked as an alternative to varying K_2. Considerable constructional and experimental difficulties arise, however. The construction of a screened variable condenser which can be varied from about $2\mu\mu$F to $20\mu\mu$F does not appear to have been solved. The high insulation resistance and small dielectric loss necessary, if useful determinations of φ_2 and $\sigma_{1\ \text{min.}}$ are to be made, will probably give great difficulty. This avenue would, however, certainly be a useful one to pursue, as it would be possible to work with a fixed known air gap, and so keep all the resonator constants invariable when the series capacity is varied.

2. The temperature coefficients of response frequency are not negligible except for longitudinal resonators of suitable shape. The coefficients are those to be anticipated from the known coefficients of Young's modulus with temperature. Further information regarding the latter could be obtained by a systematic investigation of the frequency temperature coefficients of resonators of various types and modes of vibration. Care would be needed to discriminate a possible effect due to a change in K_1 with temperature. Observations of the coefficients with the same resonator in different air gaps would serve this end.

3. The simple theory developed accounts for those effects on oscillators which are common to resonators ; it is probable that a more complete theory introducing the electrical equivalents of the valve and other associated electrical circuits would account for the further effects on frequency of oscillators consequent upon these circuits. Such effects have been studied to some extent, and are being pursued. Scope for considerable investigation exists in the case of oscillators both from the theoretical and from the experimental points of view.

A considerable future awaits development in the application of resonators and oscillators as frequency standards, filters, frequency controllers, etc. This use at transmitting stations conjointly with the production of local heterodyne frequencies by them will permit of the production of an extremely constant frequency difference. This is an application that has considerable possibilities not yet developed.

In conclusion, I wish to render thanks to Mr. Vigoureux and to Mr. Martin, who have shown much care and patience in taking many of the observations, some of which are tedious. The former has also shown much insight into the experiments, and the latter has prepared some of the specimens with skill.

The work was carried out under the auspices of the Standards Sub-Committee of the Radio Research Board, Department of Scientific and Industrial Research.

REFERENCES.

(1) The Piezo-Electric Resonator. W. G. Cady. Proc. Inst. Radio Engrs., Vol. 10, p. 83 (1922).

✓ Piezo-Electric Standards of High Frequency. W. G. Cady. Jour. Optical Soc. of America and Review of Scientific Instruments, Vol. 10, No. 4 (1925).

See also :—

An International Comparison of Radio Wavelength Standards by Means of Piezo-Electric Resonators. W. G. Cady. Proc. Inst. Radio Engrs., Vol 12, p. 805 (1924).

(2) Piezo-Electric Crystal Resonators and Crystal Oscillators Applied to the Precision Calibration of Wavemeters. G. W. Pierce. Proc. Am. Acad. of Arts & Sciences, Vol. 59, p. 82 (1923).

Piezo-Electric Crystal Oscillators Applied to the Precision Measurement of the Velocity of Sound in Air and CO_2 at High Frequencies. G. W. Pierce. Proc. Am. Acad. of Arts and Sciences, Vol. 60, p. 271 (1925).

(3) Sichtmachung von hochfrequenten Longitudinalschwingungen pfezo-elektrischer Kristallstäbe. E. Giebe and A. Scheibe. Zeitschriftfür Physik-Vol. 33, p. 335 (1925).

(4) The Structure of α and β Quartz. Sir W. Bragg. Proc. Roy. Soc. A., Vol. 160, No. 751, p. 495 (1925).

(5) Electrically Maintained Vibrations. S. Butterworth. Proc. Phys. Soc., 27[illegible]. 410 (1915).

(6) A Self-Contained Standard Harmonic Wavemeter. D. W. Dye. Trans. Roy. Soc., Vol. 224, p. 259 (1924).

(7) The Electrical Network Equivalent of a Piezo-Electric Resonator. K. S. Van Dyke. Phys. Rev., Vol. 25, No. 6, Abs. No. 52, p. 895, June (1925).

It has been worked out from first principles that the constants of the network (in terms of the nomenclature used in the present Paper) are as follows :—

$$N = M/4\varepsilon^2 b^2,\ K = 4\varepsilon^2 b^2/g,\ S = N_1/4\varepsilon^2 b^2$$

$$\text{and } K_1 = \left(\frac{k}{4\pi} - \delta\varepsilon\right)\frac{bl}{e}$$

where M, N_1 and g are the equivalent mass, frictional coefficient and stiffness of control,

δ is the modulus of elasticity, and

ε is the piezo-electric constant in c.g.s. and electro-static units.

(8) New Method of High Frequency Resistance Measurement. E. Mallett and A. D. Blumlein. Inst. El. Eng. J., 63, p. 397 (1925).

Also :—

(9) The Quartz Oscillator. E. Mallett and V. J. Terry. Wireless World and Radio Review, 16, p. 630 (1925).

(10) Piezo-Electrically Induced Vibrations in Quartz Rods. M. v. Laue. Zeitschrift für Physik, Vol. 34, p. 347 (1925).

DISCUSSION.

Dr. **Ezer Griffiths** : I am interested in the practical applications of the piezo-electric crystal oscillator, as it has great possibilities. When I saw the Paper by Pierce on the precision measurement of the velocity of sound in air and CO_2 at high frequencies it occurred to me that a gas analysis instrument could be based on this principle. Such an instrument would have the advantage of not disturbing the chemical composition of the atmosphere under test. I have made a rough trial of the method for the determination of the percentage of CO_2 in a mixture of air and CO_2, and for this purpose Mr. Dye kindly supplied me with the quartz oscillator shown, which gives out longitudinal waves of frequency about 40,000 per second. The instrument has given promising results. Many other applications can be found for this useful tool, especially in thermal measurements. It is curious to note that piezo-electricity has been known for about 45 years, and that it is only within the last few years that the effect has been turned to practical account.

Dr. D. **Owen** said that the Paper, like the author's previous contribution dealing with the cathode ray oscillograph, is quite an exceptionally beautiful application of physics and a justification of the phrase " the fairyland of science." He wished Professor Boys, who first discovered the mechanical properties of quartz, could have been present to hear the Paper. The observations relating to the temperature coefficient of natural frequency show that in one case the author can control the frequency to 1 part in 100 million, while the temperature coefficient itself in no case exceeds 1 part in 10,000 per degree. The question as to the cause of the differences in the temperature coefficients, which the author discusses towards the end of his Paper, offers an attractive field for inquiry.

Mr. R. S. WHIPPLE said that, apart from the great beauty of the scientific work described in the Paper, physicists are much indebted to the author for establishing the extraordinary constancy of Pierce's circuit for maintaining oscillations, which is of the greatest industrial importance.

Dr. E. H. RAYNER said that the author had shown him a crystal sent to the National Physical Laboratory for testing, which had the peculiarity that it exhibited some scores of different natural frequencies, a very striking property in a crystal the size of a sixpence. He also mentioned that the Radio Research Board, at whose instance the work had been undertaken, had adopted the unusual course of releasing the Paper for publication by the Society before they had themselves considered it, on account of its exceptional importance.

The PRESIDENT expressed the thanks of the meeting to the author and to the Radio Research Board.

XXXIX.—THE CURRENT-VOLTAGE CHARACTERISTICS OF ELECTROSTATIC MACHINES WHEN SUPPLYING CURRENT TO NON-INDUCTIVE LOADS AND TO A COOLIDGE X-RAY TUBE.

By EVAN J. EVANS, *M.Sc.(Lond.)*, Sir John Cass Technical Institute, London.

Received May 18, 1926.

SUMMARY.

Experiments are described in which a large electrostatic machine is used as a source of potential for the discharge through (*a*) a Coolidge X-ray tube, and (*b*) a non-inductive resistance. The results are represented in the form of characteristic curves. In the former case it is shown that above a certain critical voltage the discharge is intermittent, while in the latter case the discharge is continuous for all voltages.

The cause of the intermittence of the current through the Coolidge tube is assigned to the operation of the Pearson-Anson effect, and this implies the conclusion that the effect of the residual gas in such tubes is not completely insensible above a certain voltage.

§ 1. *Introduction.*

WHEN an electrostatic machine is driven at constant speed it is generally assumed that it provides a source of constant electromotive force, capable therefore of generating a steady direct current at a constant difference of potential. There appears, however, to be little definite evidence on the question. In Sir J. J. Thomson's "Conduction of Electricity Through Gases" (2nd edition, p. 514) it is stated that a large electrostatic machine gives a continuous discharge, and in proof reference is made to a Paper by Strutt.* Curiously, no mention whatever occurs in this Paper of the use of an electrostatic machine. In a Paper† read before this Society in 1923 an experiment was described, and an actual photograph was shown, from which it was inferred that the current through a Coolidge tube supplied by an electrostatic machine was intermittent. Since the cause of the intermittence might reside in the properties *either* of the Coolidge tube *or* of the electrical machine itself, it was obviously desirable to seek direct evidence as to the constancy of the discharge from an electrical machine when connected to a purely ohmic resistance.

Experiments have been carried out on two large machines, one a 20-plate sectorless machine of the Bonetti type, with ebonite plates 22 in. in diameter; the other a machine of the Holtz pattern, with 16 movable glass plates 36 in. in diameter. In the first place it was found that when the load is a non-inductive ohmic resistance the current is steady, showing no sign of intermittence at any value of the terminal voltage. This point having been ascertained, it was possible to proceed to the determination of the external characteristic of the machine, expressed as a curve with P.D. across the terminal as ordinate, and the steady load current as abscissa. So far as the author is aware, such characteristics have not been described before. Wommelsdorf‡ has published data respecting electrical machines in the form of curves to which he applied the term *characteristic*, the currents being expressed in terms of the number of sparks per second supplied to a Leyden jar of known capacity.

---

* Strutt, Phil. Mag., Vol. 48, p. 478 (1899).

† Harlow and Evans, Proc. Phys. Soc., Pt. 4, pp. 9D-25D (1923).

‡ Wommelsdorf, Phys. Zeitschr., December (1904).

Each single observation of this kind involves a series of rises and falls of potential, and it is clear that his curves are in no way comparable with the simple characteristics by which, for example, the action of a direct-current dynamo is usually represented, and which are analogous to those described in the present Paper in relation to the electrostatic machine.

The characteristics obtained are found to consist of two fairly marked stages. As the current gradually increases from zero the curve falls steeply, and is convex towards the origin. A point of inflexion marks this off from the second stage, in which the curve rapidly becomes vertical, so that practically no change of current occurs as the P.D. drops to zero. In the glass plate machine inflexion occurs at a potential of about 45 kilovolts ; in the ebonite plate machine at about 20 kilovolts.

Experiments were next made when the load on the machine was a Coolidge X-ray tube. Plotting spark-gap potentials against mean currents, the resulting characteristics were found to differ materially from those found on purely ohmic loads—a fact admitting of only one interpretation, namely, that the current through the Coolidge tube is fluctuating or intermittent. This applies only at the upper voltages, namely, above 35 kv., the currents through the Coolidge tube in this region being distinctly less—down to a half or a third—of the values of the current through a water resistance at the same terminal voltage. Below the critical value of the voltage the characteristics on the Coolidge tube and on the ohmic resistance are indistinguishable.

The probable cause of the intermittence is assigned to the operation of the Pearson-Anson effect. This implies the conclusion that the effect of the residual gas in a Coolidge tube is not insensible above a certain critical voltage, which, it is suggested, is the sparking potential of the gas under the conditions prevailing in the tube.

I. THE CHARACTERISTIC OF THE ELECTROSTATIC MACHINE ON NON-INDUCTIVE LOADS.

§ 2. *Steadiness of Terminal Voltage.*

In order to solve the problem as to the constancy of the current supplied by an electrostatic machine to a non-inductive ohmic resistance, observations were made with the circuit indicated in Fig. 1. The non-inductive resistances used, represented by *R*, consisted of water resistances. These were columns of freshly distilled water in glass quill-tubing, a metre or more in length, bent twice at right angles. The tubes, provided with platinum electrodes at various points along their lengths, were first cleansed by successive washings with distilled water, and after a final filling with distilled water the ends were closed with rubber caps. By using a few tubes a sufficient number of resistances were rendered available, covering the range from 100 to 1,000 megohms.

The corresponding range of P.D. across the terminals of the electrostatic machine was 20 to 90 kilovolts. These voltages were measured by the sphere spark-gap, consisting of a pair of polished brass balls *SS′* 5 cm. in diameter, at a variable and measurable distance apart, a high resistance being placed in series to prevent surges. The values of P.D. in terms of spark length were taken from Kaye and Laby's Tables of Physical Constants.

One terminal *A* of the machine *M* was earthed. Currents were measured by a micro-ammeter *G* inserted in the earthed lead. Various changes were made to check the possibility of part of the current through G being due to brush discharge, so as to ensure that the current recorded was actually that passing through the resistance R.

The theoretical basis of the measurements is as follows: The spark-gap value gives the peak potential across R, while the micro-ammeter measures the mean value of the current through it. If the quotient of peak potential by mean current agrees with the value of R given by ordinary low-voltage methods, it follows that the current supplied by the machine must be perfectly steady. If, on the contrary, this quotient should exceed the value of R found by the usual steady current methods, the conclusion to be drawn is that the applied voltage, and consequently the current through a non-inductive resistance, is variable or intermittent.

The method used to determine the value of R was to charge a 1/3 microfarad standard condenser to 200 volts, then measure the time of fall to half value when its terminals were connected through the resistance under test. An electrostatic voltmeter across the condenser indicated the voltages. This measurement was made both before and after an observation with the electrostatic machine.

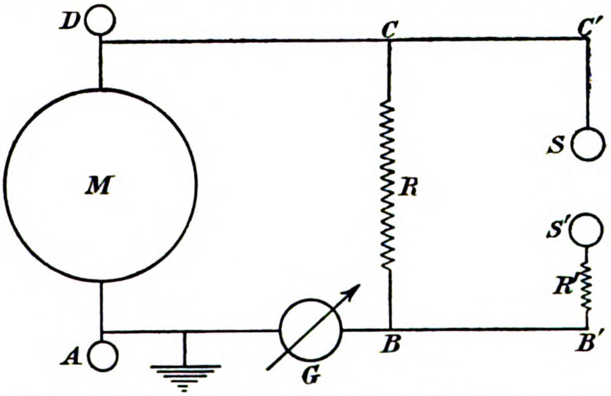


Fig. 1.—Circuit for Testing Steadiness of the Current Supplied by an Electrostatic Machine to a Non-Inductive Ohmic Resistance.

A representative set of results is shown in Table I. These results show a satis-

Table I.—*Test of Invariableness of the Current Supplied by an Electrostatic Machine on Non-inductive Loads.*

Spark Gap (cm.).	Kilovolts (deduced from spark gap).	Mean Current (milliamp.).	$\frac{\text{Kilovolts}}{\text{Milliamp.}} \div 10^6$	R (megohms).	Percentage Difference.
0·625	21	0·195	108	109	−1·0
1·42	42	0·321	130	126·7	+2·5
1·69	49	0·276	177	178	−0·7
1·93	54	0·227	238	237	+0·3
2·15	59	0·110	534	537	−0·6
2·35	63	0·190	331	326	+1·5
2·50	66	0·269	239	238	+0·4
2·76	69	0·188	378	381	−0·8
2·80	70	0·305	236	237	−0·4
2·95	75	0·158	475	474	+0·2
3·56	85	0·121	703	712	−1·3

factory agreement between the quotient of peak volts and mean amperes, and the values of the resistance R. The conclusion is that, over the whole range of voltages used, large electrostatic machines supply a perfectly steady voltage and current to a non-inductive ohmic resistance. An accuracy of 2 to 3 per cent. in the observations was aimed at throughout.

§ 3. *Characteristics on Non-inductive Load.*

The constancy of voltage and current on non-inductive loads being established, it is possible to obtain experimentally the external volt-ampere characteristic of a machine. In conducting the measurements a high-resistance voltmeter V was sometimes substituted for the spark-gap method of measuring potential differences, the connections being as in Fig. 2, in which R denotes the variable part of the load, while R_s is a constant water-resistance in series with a millivoltmeter. The form of the characteristic obtained for a particular machine, depending as it does on atmospheric conditions, is no strictly reproducible curve, but varies from day to day, and even sometimes in the course of a single run. Characteristics obtained at different times agree, however, in general type. Two fair samples, one for the glass plate machine and one for the ebonite plate machine, are shown in Figs. 3 and 4; and the data in one case are shown in Table II.

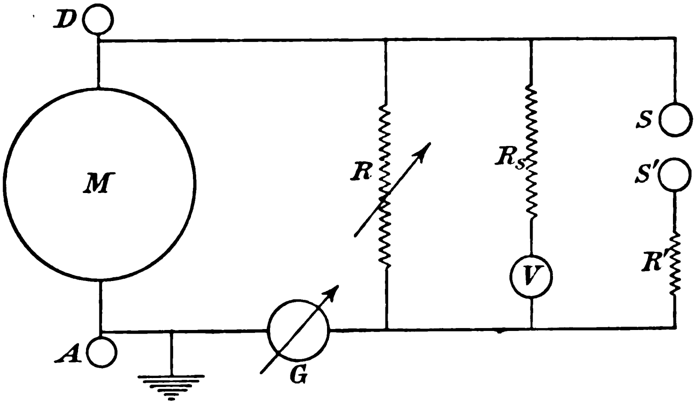


FIG. 2.—CIRCUIT CONNECTIONS WHEN DETERMINING CHARACTERISTIC OF ELECTROSTATIC MACHINE ON NON-INDUCTIVE LOADS.

TABLE II.—*Characteristic of Bonetti Machine.*

Kilovolts.	Milliamps.
66	0·065
58	0·095
40	0·190
30	0·30
25	0·375
16	0·395
10	0·402
0	0·402

These characteristics will be seen to possess the special features already described in the introductory section.

The readings for the lowest voltages were obtained by considerably reducing the external resistance, and finally short-circuiting the terminals of the machine.

When the machine is short-circuited the current gradually dies down to zero. A typical decay curve is shown in Fig. 5.

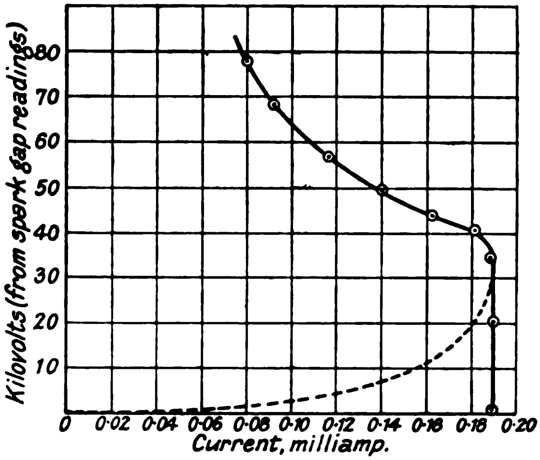


FIG. 3.—CHARACTERISTIC OF ELECTROSTATIC MACHINE (HOTTZ TYPE, 16-PLATE, DIAMETER 36 INS., GLASS) ON NON-INDUCTIVE LOAD.

(The dotted curve suggests the form of the characteristic when traversed infinitely slowly.)

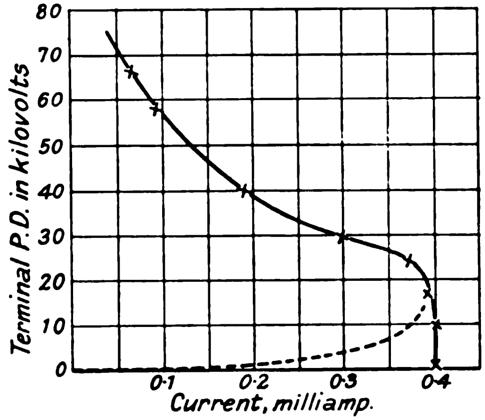


FIG. 4.—CHARACTERISTIC OF ELECTROSTATIC MACHINE (BONETTI TYPE, 20-PLATE, DIAMETER 22 INS., EBONITE) ON NON-INDUCTIVE LOAD.

(The dotted curve suggests the form of the characteristic when traversed infinitely slowly.)

It thus appears that when the terminal voltage becomes very low an electrostatic machine gradually becomes de-excited. In the strictly steady state the characteristics would be probably of the form suggested by the dotted lines of Figs. 3 and 4. They are reminiscent of the external characteristic of a shunt dynamo for very low values of the external resistance.

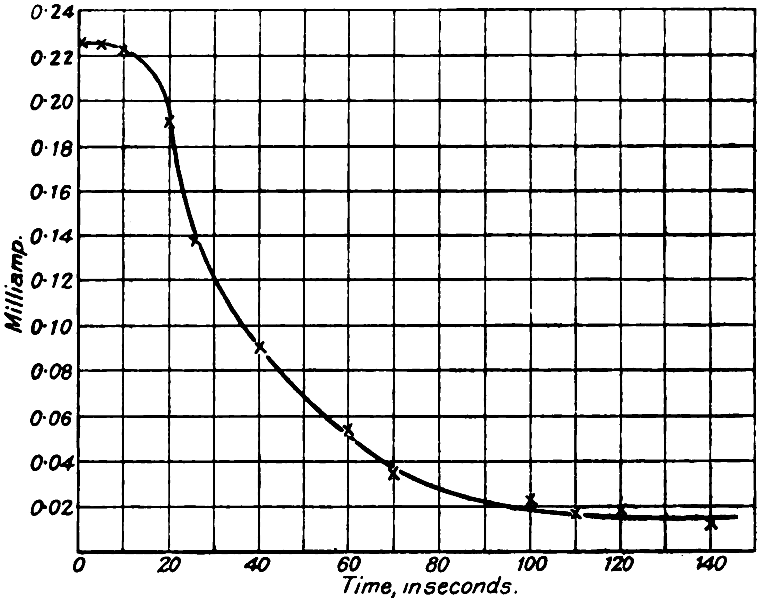


FIG. 5.—DECAY OF SHORT-CIRCUIT CURRENT OF ELECTROSTATIC MACHINE WITH TIME.

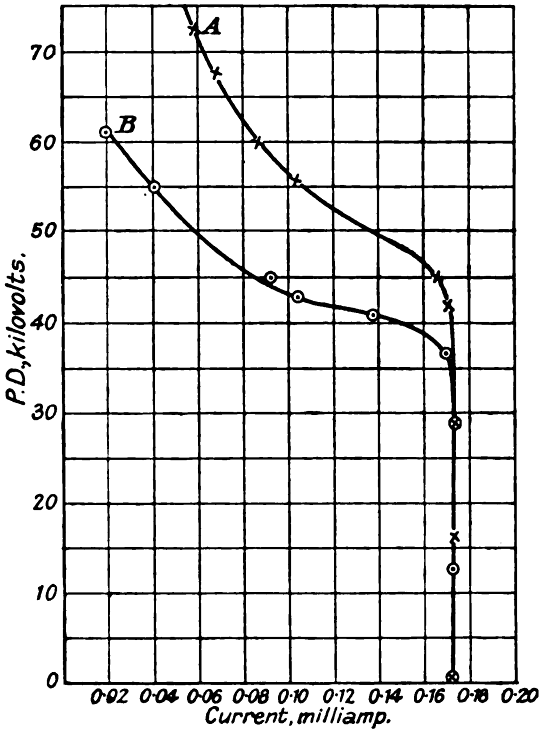


FIG. 6.—CHARACTERISTICS OF ELECTROSTATIC MACHINE.

A. On non-inductive ohmic loads.

B. On Coolidge Tube (for a series of values of filament heating current).

II. Characteristic of an Electrostatic Machine with Coolidge X-Ray Tube as Load.

§ 4.

Observations on the same lines as those above described were made, the Coolidge tube taking the place of the water resistances. The circuit connections were as in Fig. 1, with the difference that the Coolidge tube could be substituted for the water resistances. Voltages were measured by the spark-gap method, and mean current by the moving-coil micro-ammeter.

With the Coolidge tube in circuit, various points on the external characteristic were obtained by using successive values of filament heating current. If the current from cathode to anode of the tube is quite steady, the volt-ampere curve is bound to coincide with the characteristic obtained on ohmic non-inductive load. The curves actually obtained, however, were found to have a special character of their own. In order to eliminate differences arising from accidental variations in the action of the machine, the experimental procedure adopted was to take three characteristics in succession, the first and third in order of time being on water resistances, the middle one on the Coolidge tube. A typical set of observations is given in Fig. 6, the corresponding numerical data being given in Tables III and IV.

Table III.—*Coolidge Tube Loads.*

Kilovolts.	Ammeter Reading.
55	0·041 milliamp.
37	0·173 ,,
61	0·014 ,,
29	0·173 ,,
42·5	0·104 ,,
16·5	0·173 ,,
41	0·138 ,,
43	0·104 ,,
45	0·083 ,,
0	0·173 ,,

Table IV.—*Non-inductive Loads.*

Kilovolts.	Ammeter Reading.
72·5	0·059 milliamp.
60	0·086 ,,
56	0·104 ,,
45	0·166 ,,
42·5	0·173 ,,
68	0·069 ,,
18	0·166 ,,
16·5	0·173 ,,
0	0·173 ,,

For the smaller current values the Coolidge characteristic falls definitely below that on non-inductive load. As the current increases the two curves approximate, and the final vertical portions coincide exactly.

The cause of the distinction between the two characteristics cannot remain in doubt. It has been shown in § 1 that on non-inductive ohmic loads both current and voltage are quite steady for any given load. We are therefore led to the conclusion that at the higher voltages the current taken by the Coolidge tube is fluctuating or intermittent, whilst at the lower voltages the current through the tube is steady. The critical value of the voltage is found to be about 35 kilovolts.

§ 5. *Confirmatory Experiments.*

To confirm the conclusion that for applied voltages exceeding 35 kv. the current supplied by an electrostatic machine to a Coolidge tube is intermittent, the following experiment was made: In parallel with the Coolidge tube was placed a water resistance of value 750 megohms, with a micro-ammeter in series. By varying the filament current the current through the tube, and accompanying this, the P.D. across the machine terminals was made to vary, so that a set of readings was obtained connecting the mean current through the 750 megohm resistance and the voltage across it as measured by the spark gap. The results are shown in Fig. 7.

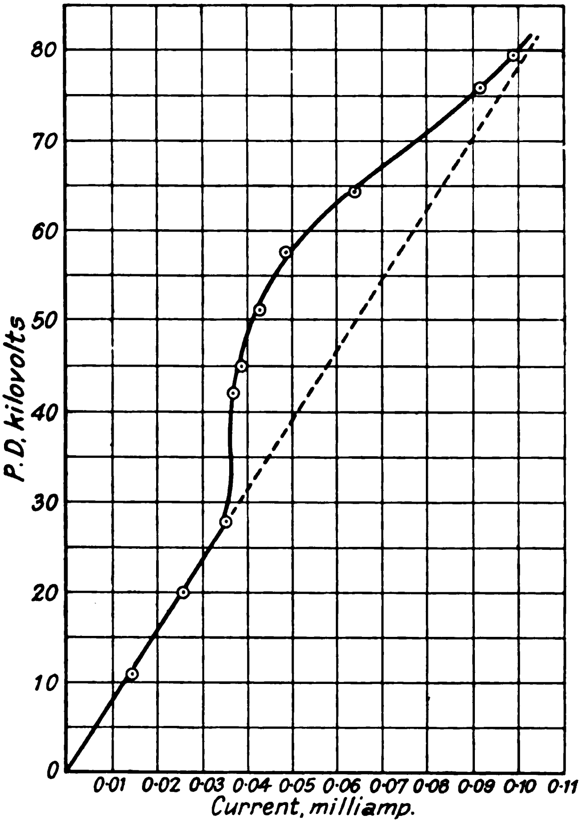


FIG. 7.—VARIATION WITH PEAK VOLTAGE OF THE MEAN CURRENT THROUGH A 750 MEGOHM WATER RESISTANCE PLACED IN PARALLEL WITH A COOLIDGE TUBE ACROSS AN ELECTROSTATIC MACHINE.

It will be seen that below about 35 kv. the observations lie on the straight line, making with the axis of current an angle whose tangent is equal to the resistance of the water tube. Above that critical value of the voltage, however, the current begins to fall below that corresponding to steady voltages, showing that the current is now intermittent. The deviation reaches its greatest value at about 50 kv., the mean current being then less by 33 per cent. than that due to a steady voltage equal to that measured by the spark gap. As the voltage rises still higher the observations again approach the initial straight line, as is to be expected, since with rise of voltage the current through the tube falls, while the current through the fixed resistance rises. Placing a Coolidge tube in parallel with a non-inductive resistance thus causes the current through the latter to become intermittent ; this can only be a consequence of the fact that the current through the Coolidge tube is itself intermittent, it being borne in mind that the electrostatic machine behaves as if it possesses a large internal resistance.

Thus the conclusion is confirmed that at a potential difference exceeding a certain critical value, about 35 kv. for the tube used, the current through a Coolidge tube is intermittent, while below that value the current through the tube is steady ; the voltage being in all cases supplied by an electrostatic machine.

Further attempts were made to observe the effects of intermittence by connecting in series with the Coolidge tube a wireless receiving coil of several hundred turns, magnetically coupled to a similar coil in a secondary circuit containing also a rectifying crystal and a galvanometer. Preliminary calculation led to the expectation of a just detectable rectified current in the secondary circuit. The effect of the slight sparking at the collectors of the machine tends, however, to mask the results, and although deflections were obtained they could not be regarded as decisive.

§ 6. *Remarks on the Cause of Intermittence of Current in the Coolidge Tube.*

The existence of intermittence or fluctuation in the passage of electricity through gases is a phenomenon which has been long recognised. There appears to be several distinct types of this effect. There is the effect discovered by Whiddington,* where the action is of a simple nature, the fundamental frequency of intermittence being proportional to the square of the voltage applied to the electrodes, and determined entirely by the conditions within the tube itself. More recently Appleton and West† have recorded observations of the phenomenon to which they apply the term ionic oscillation, associated with the striated discharge ; the effect being here also apparently independent of conditions external to the tube. The most usual cause of intermittence, however, appears to reside in the Pearson-Anson‡ effect, in which the period of intermittence of current through the discharge tube is controlled by resistance and electrostatic capacity external to the tube.

In regard to the effect in the Coolidge tube described in the present Paper, the explanation that appears most probable is on the lines of the last-named effect. It involves the assumption that an appreciable, though not large, fraction of the current through a Coolidge tube is, for voltages exceeding a certain critical value, carried by the residual gas in the tube ; the remainder of the current being carried by the pure electronic emission from the cathode. The critical voltage may be identified with the sparking potential of the gas in the tube. The terminal P.D. of an electrostatic machine giving 150 kv. on open circuit appears to drop to half value when a water resistance of 1,500 megohms is placed in circuit with it. Assuming, then, an effective internal resistance of 1,500 megohms in the machine, and an estimated capacity of $50 \mu\mu$F. due to the machine terminals, Coolidge tube and connections, a period of intermittence of the order of 0·075 second is to be expected—that is, a frequency of about 13 per second. This is of the order of frequency indicated in the photograph recorded by Harlow and Evans (loc. cit.).

---

* Whiddington, Radio Review, November (1919).

† Appleton and West, Phil. Mag., May (1923).

‡ Pearson and Anson, Proc. Phys. Soc., Vol. 34, p. 204 (1922).

This result is apparently in opposition to the usual view that the current through a Coolidge tube is due to the purely electronic emission. It should be noted that the value of the mean current found in the present experiments does not fall below one-half, or at most one-third, of what would be expected if the current were quite steady. In the Paper* in which Coolidge announced the production of his tube it may be pointed out that the very experiments there cited as leading to the conclusion that the discharge is purely electronic point to a systematic drop in the current through the bulb, down to something near half value as the voltage across the tube is *increased.*

It is surely not surprising that the residual gas in a Coolidge tube should make its presence felt to some extent. For, assuming the vacuum to be a few hundredths of a micron (as Coolidge supposes), there would still be some 10^{12} molecules per c.c. left. These molecules are subject not only to the fierce bombardment of the electrons emitted from the hot cathode, but also to the ionising effect of the intense X-radiation in the immediate vicinity of the focal spot on the target. The gas might therefore be expected to take some share in the production of current, this being, of course, necessarily attended by the production of positive ions.

In conclusion, it may be recalled that the results recorded in this Paper also serve to account for the fact that the output of X-rays from a Coolidge tube driven by an electrostatic machine is, if anything, inferior in intensity and hardness to that obtainable when using the rectified voltage from an alternator with step-up transformer, the spark-gap voltage in each case being the same; a result very difficult to reconcile with the assumption that in the former case the voltage remains perfectly steady. The existence of intermittence brings into play a double effect; it reduces the total output of X-radiation, and at the same time degrades the average hardness of the rays produced.

My thanks are due to the Senate of the University of London for grants made from the Dixon Fund; to the Medical Supply Association for their readiness to place electrostatic machines at my disposal; to the Principal and Governors of the Sir John Cass Institute, at the Physics Department of which this work was carried out; and also to Dr. D. Owen for his great interest and valuable advice and help in the work.

DISCUSSION.

Major C. E. S. PHILLIPS said that all who are interested in medical X-ray work would welcome this investigation, because practitioners now aim at constant conditions of voltage, and the subject is therefore of considerable practical importance. A modern outfit for supplying the high voltages employed is expensive and bulky; a less elaborate source, giving an E.M.F. in the neighbourhood of 300,000 volts, is greatly needed, and perhaps the Paper would lead some inventor to produce a satisfactory modification of existing electrostatic machines. It seemed very surprising that a Coolidge tube, whose resistance is constant to 1 per cent. with a transformer, should give rise to intermittent current with a machine. Had the author experimented with different types of tube.

---

* Coolidge, Phys. Review, Vol.2, pp. 409, 430 (1913).

such as a large-volume deep-therapy tube and a radiator tube ? It might even be worth while to study the effect of admitting a little gas.

The PRESIDENT said that he should be sorry to think that all Coolidge tubes were subject to residual gas effects, but he had often suspected these in tubes of the radiator type used by the author.

Mr. R. M. ARCHER (communicated) : As one who realises the uphill nature of evening research work I would like to congratulate the author on his producing such an interesting Paper. I have had many chances of seeing his experiments and can support his remarks regarding the difficulty of getting his machines to repeat characteristics consistently. Would it be practicable to enclose them in a kind of greenhouse and to maintain the hygrometric and pressure conditions approximately constant ? In any case I think it would be worth while to find the dew-point and to record pressure and temperature.

The water-tube resistances are regarded as non-inductive. But has any capacity effect—due, say, to films of moisture on the outer surface of the glass—been noticed ? Has the author thought of using some type of oscillograph in any future work ? In view of the importance of the research I think the expense would be justified.

Dr. D. OWEN (communicated) : The author has carried out experiments which throw light both on the action of an electrostatic machine of the Wimshurst type, and on the actions within a Coolidge X-ray tube. The experiments with non-inductive ohmic resistances show in a straightforward way that the discharge of a large electrostatic machine on such a load is essentially at steady potential. The characteristics obtained with a Coolidge tube as load show such a marked difference, compared with those on resistances satisfying Ohm's law, that it is difficult to resist the conclusion that the discharge in the former case is no longer continuous.

The author attributes the intermittence or fluctuation to the Pearson-Anson effect. The fact that the present experiments reveal the existence of a critical voltage, and that in previous work a definite frequency of inconsistence of the X-rays was observed on a photographic plate certainly seem to favour this explanation. But on the other hand the Pearson-Anson effect is usually seen in a gas discharge at comparatively high pressure, and the existence of this effect in a highly exhausted tube is quite problematical. It requires a very high resistance in series with the tube, and it is possible that whilst the effect occurs when an electrostatic machine is used as generator it may not do so when an induction coil or transformer is substituted.

If the gas in the Coolidge tube takes part in the discharge, the question of the manner of this arises. Taking the current due to gaseous ionization to be of the order of a milli-ampere, as the recorded observations suggest, then the number of univalent ions flowing per second is 5×10^{15}. If the volume of the tube be taken as a litre, and the gas pressure as 10^{-5} mm., then the total number of molecules of gas present is only $3{\cdot}6 \times 10^{14}$. But it must be remembered at the high voltage present, combined with the low pressure, the velocity acquired even by positive ions is very high, so that a gas molecule may be ionized, take part in the discharge and be liberated again from the cathode very many times in one second. Further, the impacts of these ions on the hot cathode will raise its temperature locally and so enhance the pure electronic discharge. The blackening of the bulb of a Coolidge tube may perhaps be due to slow disintegration of the cathode arising thus. In such ways it is possible to picture the minute amount of residual gas producing sensible effects upon the discharge through the tube.

Author's reply : I have not been able to carry out any work with tubes other than those of the radiator type. I have, however, experimented with two radiator tubes, such as are used in X-ray practice. In all the experiments it was found necessary to keep the filament current at about 70 per cent. of that for which the tubes were rated.

With regard to Mr. Archer's suggestion of a " greenhouse " it may be stated that one of the electrostatic machines used was enclosed in a glass case, the air in which was dried by means of sulphuric acid. Records of hygrometric states of the surrounding air, pressure, etc., were kept in some of the early experiments, but no satisfactory information was obtained.

No capacity effects were noticed with the resistances used. An oscillograph, if a suitable one had been available, would have undoubtedly been of very great advantage.

XL.—THE REFRACTION AND DISPERSION OF GASEOUS CARBON DISULPHIDE.

By H. Lowery, *M.Sc., A.Inst.P., F.R.A.S.*, Lecturer in Physics, Technical College, Bradford.

Received May 20, 1926.

I. Introduction.

THE following values of the refraction and dispersion of gaseous carbon disulphide are as recorded by Dufet,[*] who summarised the data up to the year 1900. No further determinations seem to have been made since that date.

λ	$(\mu-1)\times10^6$ at 0°C. and 76 cm.	Observer.
White	1524	Arago[†]
White	1497	Dulong[‡]
D	1476	Mascart[§]
Li	1460	Lorenz[‖]
D	1480	Lorenz

In view of these incomplete data, it was considered desirable to commence an investigation on the refraction and dispersion of gaseous compounds with measurements on carbon disulphide.

II. Experimental.

For the purpose of this work a Jamin interferometer was mounted.

As source, a " point-o-lite " was employed in conjunction with a Hilger constant deviation spectroscope, in which the eyepiece of the telescope was replaced by a second slit. It was thus possible to obtain light of different wavelengths for the experiments on dispersion.

The light leaving the spectroscope was focussed on the slit of a collimator, which directed parallel light on the first plate of the interferometer. The interference bands were observed through a telescope directed towards the second plate.

The refraction tubes were of glass, about 45 cm. long, provided with optically worked glass ends. They were mounted in a tank which stood on a table between the interferometer plates. Water at a constant temperature of 30°C. surrounded the tubes during the experiments, the temperature being controlled by a thermostat. Precautions were taken to screen the plates of the interferometer from the heat of the tank of warm water.

Whilst measurements were being carried out one of the refraction tubes was kept exhausted of air. The other tube was in communication with a reservoir containing pure liquid carbon disulphide initially cooled by being immersed in a vessel of solid carbon dioxide. It was first exhausted of air, and then carbon disulphide vapour was allowed to pass into it as the temperature of the reservoir gradually rose to about 20°C.

---

[*] Recueil des Données Numériques, Vol. I.

[†] Mem. Sci., t. II, p. 711, Paris (1859).

[‡] Ann. de Ch. et Phys. (2 Ser.), t. XXXI, p. 154 (1826).

[§] Comptes Rendus, LXXXVI, p. 321 (1878).

[‖] Wied. Ann., XI, p. 70 (1880).

Both refraction tubes were connected to mercury manometers. A density bulb communicated with the carbon disulphide apparatus, and was immersed in the tank with the tubes.

The number of interference bands passing a spider line in the telescope was counted whilst the vapour entered the refraction tube. It was found quite easy to read to one-tenth of a band.

Pure liquid carbon disulphide was supplied by Messrs. Woolley, Sons & Co., Ltd., of Manchester.

III. RESULTS.

Previous observers have frequently pointed out the artificial nature of results of refractivity determinations reduced to N.T.P. conditions in the case of vapours which do not obey the gas laws. It is more satisfactory to consider the refractivity in connexion with the density as has been done, for example, by Le Roux,* Lorenz,† Prytz‡ and Cuthbertson.§

In the present work the refractivity and dispersion have been determined as in the experiments of Cuthbertson, and the results are expressed in connexion with the density determinations.

(*a*) *Refractive Index of Carbon Disulphide Vapour.*

The refractive index of carbon disulphide vapour was determined for the green mercury line (λ 5461) in 10 experiments, in each of which about 200 bands were counted, the difference of pressure between the refraction tubes not exceeding 14 cm. of mercury.

The following values were obtained, reduced so as to show the refractivity of carbon disulphide vapour by the same number of molecules as 1 c.c. of hydrogen contains at N.T.P. :—

$(\mu-1)\times10^6$ 1477, 1481, 1472, 1482, 1472,
1475, 1476, 1480, 1473, 1480
Mean ...... 1477 (λ 5461).

The data employed in obtaining the above reduced values were: C=12·000, H=1·008, S=32·064 and density of hydrogen=0·08985 grams per litre. These give the theoretical density of carbon disulphide vapour as 3·393 grams per litre. The density of carbon disulphide vapour is given in the usual collections of physical tables relative to that of air. From the present experiments, the mean density of carbon disulphide vapour is 3·451 grams per litre, the reduction being effected by the expression

$$d=d_0 \cdot \frac{(t+273)}{273} \cdot \frac{760}{p}$$

where d is the reduced density, d_0 the observed density at pressure p mms. of mercury and temperature t°C.

---

* Ann. de Ch. et Phys. (3 Serie), LXI, p. 385 (1861).
† Wied. Ann., XI, p. 70 (1880).
‡ Wied. Ann., XI, p. 104 (1880).
§ Proc. Roy. Soc., A, Vol. 97, p. 152 (1920), and references.

Merely for the sake of facilitating comparison of the results of the present work with those given above by Mascart and Lorenz, the refractive index of carbon disulphide vapour was determined for sodium light ($\lambda 5893$) in six experiments with the following results :—

$(\mu-1)\times 10^6$ ...... 1480, 1488, 1485, 1486, 1481, 1482.
Mean ...... 1484 ($\lambda 5893$).

Note.—These results are *not* reduced by considerations of density, but are the values of the refractive index reduced to N.T.P. conditions by the expression

$$(\mu-1)=\frac{n\lambda}{l}\cdot\frac{760}{p}\cdot\frac{t+273}{273}$$

n being the number of interference bands observed, λ the wavelength of the light, l the length of the refraction tubes, p the pressure difference (in mms.) between the tubes and t the temperature of the carbon disulphide reservoir. The mean value of the refractive index of carbon disulphide vapour for $\lambda 5461$, similarly reduced to N.T.P. conditions, is

$$(\mu-1)\times 10^6=1503.$$

(*b*) *Dispersion of Carbon Disulphide Vapour.*

The dispersion of carbon disulphide vapour was measured in three sets of double experiments, employing the same dispersion points as in Cuthbertson's work. The results are shown in the following table :—

λ in Å.U.	$(\mu-1)\times 10^6$		Difference.
	Observed.	Calculated.	
Li 6708	1436 4	1436 4	0
Cd 6438	1443 3	1443 1	−2
Hg 5791	1463 2	1463 3	+1
Hg 5770	1464 0	1464 1	+1
Hg 5461	1476 7	1476 8	+1
Ag 5209	1488 8	1489 0	+2
Cd 5086	1495 6	1495 8	+2
Cd 4800	1514 6	1513 9	−7

The values in the second column are those actually obtained in the experiment reduced from density considerations.

Employing the Sellmeier type of dispersion formula, the results are summarised by the expression

$$\mu-1=\frac{5{\cdot}3530\times 10^{27}}{3926{\cdot}6\times 10^{27}-n^2}$$

n being the frequency of the light $=\frac{v}{\lambda}$. v, the velocity of light, is taken as 3×10^{10} cm. per sec.

The values in the third column have been calculated from this expression.

I desire to express my hearty thanks to Professor W. L. Bragg, F.R.S., for suggesting the research, for the loan of apparatus, and for much encouragement; also to Mr. C. Cuthbertson, F.R.S., for his helpful advice and loan of apparatus; and to Principal H. Richardson and Mr. J. A. Tomkins, Technical College, Bradford, for their interest in the work.

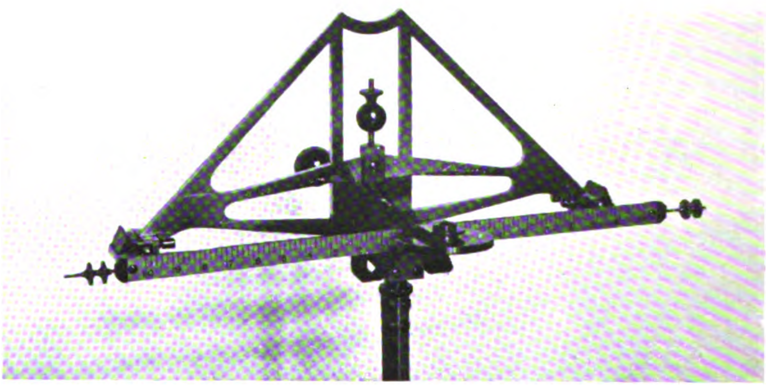


FIG. 1.

[*To face page* 473

XLI.—ON THE USE OF INVAR STEEL FOR PRECISION BALANCES.

By J. J. MANLEY, *M.A.*, Fellow of Magdalen College, Oxford.

Received May 28, 1926.

ABSTRACT.

The Paper deals with certain advantages and disadvantages which accompany the use of invar steel for the beam of a precision balance.

It was found that such a beam exhibits but little in the way of fatigue effects ; and also that its sensitivity is nearly the same for all loads.

Experiments prove that the resting-point of the balance notwithstanding the small coefficient of expansion of invar steel, may be appreciably affected by changes in temperature. This is attributed to slight relative movements amongst the several knife-edges and not to a differential lengthening of the beam itself.

The instrument is affected by magnetic storms and also by the diurnal variations in the earth's magnetism. Magnetic effects may, however, be nullified by weighing according to the method of Gauss or by a method of difference.

The conclusion reached is that provided due precautions are observed, invar steel is eminently suitable for the beams of high-grade precision balances.

AT the exhibition held by the Physical and Optical Societies in January last, Messrs. L. Oertling showed a newly designed precision balance having a beam of invar steel. This particular use of invar steel is, I believe, an innovation ; and as the behaviour of the alloy when used as a beam is of interest not only to chemists, for whom the balance is primarily intended, but also to physicists engaged upon problems involving highly accurate weighing, it seemed desirable that the new balance should be subjected to a series of tests in order that inherent merits and defects might be revealed.

Theoretically, the chief advantages offered by invar steel are high rigidity and a low temperature coefficient. Hence, given a correctly designed beam, the sensitivity will not be affected when the load is changed ; neither will the usual small temperature variations within and about the beam, appreciably alter the resting-point R.P. It is true that the known secular changes in the steel will tend to lengthen the beam : such changes are, however, exceedingly small and slow ; also in the case of short bars they are probably very uniform ; their possible effects are therefore altogether negligible.

In opposition to admitted advantages, we have the changeful influence of the earth's magnetism manifesting itself as fluctuations in the R.P. of the beam ; and to these must be added others due to purely local fields. The total effect is therefore ascertainable by direct experiment only.

For an opportunity of carrying out the necessary tests I am indebted to the makers, who, of their own initiative, very kindly offered me the loan of a new balance.

The beam, cut from a plate 2·5 mm. thick and highly polished, has the form shown in Fig. 1. Its length is 15·2 cms. and its depth at the centre 7 cms. The coefficient of expansion of the alloy which contains 36% of nickel, is 87×10^{-8}. The balance will carry a maximum load of 200 grms., and the sensitivity S as given by the makers, is ·01 mg. There is, however, no difficulty in increasing S to the value of ·003 or even more.

Before experimenting, the balance was cleaned and then placed upon a rigid support. The support consisted of a large earthenware pipe, the lower end of which was embedded in the concrete beneath the floor. To the upper end was cemented the glazed slate required for carrying the instrument. Next, the necessary adjustments were made, and the balance left undisturbed for some days. Experience shows that in this way a balance assumes its most normal condition.

For obtaining the utmost accuracy in weighing, the makers use, in addition to the ordinary scale and pointer, the now well-known device of a plane mirror attached to the beam, and a totally reflecting prism for directing the light incident from a lamp. For all the tests herein recorded, the lamp and its millimetre scale were set up at a distance of 3 ms. from the balance; the effective pointer of light was therefore 6 ms. long. The examination of the balance was in the main conducted according to methods fully described elsewhere;[*] hence much in the way of experimental detail is here omitted.

The balance having acquired a normal state was successively tested for—

- α Fatigue effects.
- β Changes in sensitivity for various loads.
- γ Influence of temperature upon the resting-point R.P.
- δ Magnetic effects.
- ε Variations due to changes in the earth's magnetism; and lastly
- η The possible effects of convection currents.

a. Fatigue Effects.—To discover whether the balance during use became fatigued,[†] various loads were tried; these ranged from 0 (empty pans) to the maximum load for which the balance was built. The effect of each load was ascertained only after the beam had been given a lengthy rest. Each experiment was started by releasing the beam, so that the amplitude of its swing approximated to the greatest value indicated by the ivory scale behind the pointer. Observations of the turning-point were commenced after the completion of the first swing, and continued until the amplitude was quite small. In this way data were obtainable for some 12 or 16, or even more, independent and successive calculations of the resting-point R.P. Finally, when the beam no longer vibrated, the actual R.P. was noted and compared with those already deduced. The R.P.'s determined vibrationally were each calculated from groups of three observations of the turning-point. Table I summarizes the results of these experiments.

From Table I it may be seen that, even if the maximum variation in the R.P. for any load be wholly assigned to fatigue effects F, the average error would still not exceed 0·02 mg. Actually, the observed differences are largely due (1) to disturbances set up when the beam is released, and (2) to irregular movements imparted to the unscreened pans by convection currents (vide infra). Hence the conclusion to be drawn from this series of tests is that the rigidity of the beam and its attachments is of the highest order. This is supported by the evidence of the next series, β.

---

[*] Phil. Trans., A, Vol. 210, pp. 387-415; and Proc. Roy. Soc., A, Vol. 86, pp. 591-600.

[†] Phil. Trans., A, Vol. 210, p. 399.

TABLE I.

Sensitivity $S=146$.

Fatigue, F.	Load.	No. of determinations.	Resting-Point, R.P.				
			Mean.	Max.	Min.	Average diff. from mean value.	R.P. (static).
Mg.	Grms.					Mg.	
0·0308	0	16	302·6	305·3	300·8	±0·4 = ±0·0027	302·5
0·0192	10	14	227·6	228·8	226·0	±0·33 = ±0·0023	228·5
0·0192	20	16	248·4	249·8	247·0	±0·26 = ±0·0018	Not observed
0·0089	50	15	287·2	287·8	286·5	±0·14 = ±0·0010	287·0
0·0240	100	13	227·1	228·5	225·0	±0·43 = ±0·0029	228·0
0·0137	200	14	243·9	245·3	243·3	±0·20 = ±0·0014	242·5
0·0193	= mean.						

The period of 1 vib. varied from 33″-65″.

β. *The Sensitivity S for Different Loads.*—For obtaining definite information concerning the sensitivity S, the position of the gravity bob was adjusted so that S acquired a value approximating 300. S was then determined for a series of loads with the following results :—

TABLE II.

Load.	0	2	4	5	10	20	50	100	200 grms.
S.	274	284	300	305	302	297	306	309	310 per 1 mg.

Neglecting for the moment the values of S for the loads 0 and 2, we note that for all loads of 4 grms. and more the average sensitivity is 304, the mean variation being $\pm 4 = \pm 0{\cdot}013$ mg. With regard to the first and second values, it seems quite clear that as the load is increased from 0 to 4 slight readjustments occur ; and that for all loads ranging from 4 to 200 grms. the relative positions of the beam and its attachments are retained almost rigidly. It may be observed that, for the balance under discussion, S would have been rendered very nearly constant by the simple expedient of increasing the weight of each pan by 4 grms. It is believed that, apart from the values of S for the loads 0 and 2, the deviations from the mean value of 304 are mainly due to the irregularities named in the preceding section α and dealt with in the concluding section η.

γ. *Temperature Effects.*—We know that the R.P. of a balance may vary with the temperature. It is difficult to account for such changes on the assumption that each arm of the beam possesses a distinctly different coefficient of expansion ; and this must be evident when we reflect upon the care exercised in the preparation and selection of the alloy. The variations in the R.P. are, however, readily understood if we grant that a changing temperature brings about small relative movements amongst the several knife-edges. Now, if this view be correct, it will be seen that, even when the material composing the beam possesses a zero coefficient of expansion, it does not follow that the balance will be free from temperature effects, and so retain a constant R.P. value ; hence the necessity for the experiments described below. It was desirable owing to the magnetic nature of the beam that these further experiments should be carried out rapidly and within a period during which the dipping needle was almost quiescent. As it could not be known when the magnetic elements would be favourable, a day was chosen at random, and by chance it proved eminently suitable (vide infra). The experiments were conducted as follows :—

First, each pan was loaded with 100 grms., the beam released and the small room in which the balance stood cooled down as much as possible overnight. The R.P. and the temperature of the beam case were determined on the following morning. Next, the temperature of the room was slowly and continuously increased and from time to time both the R.P. and the temperature of the beam re-observed. Readings were thus obtained for a range of 6·1° C. They are given in tabulated form below.

TABLE III.

R.P.	214	217	219	220	220	219	216	219	220	223	225	227 mm.
Temp.	13·3	14·0	14·6	15·1	15·5	16·0	16·9	17·5	18·2	18·7	19·0	19·4°C.

Maximum difference in temperature = 6·1°C.
Maximum difference in R.P. = 13.
Mean R.P. = 220.
Mean variation in R.P. per 1°C. = ±2·6 = ±0·008 mg.

All the above R.P. values were measured statically and not as is usual, vibrationally ; in no case was the beam arrested. Thus minute relative displacements of the knife-edges, rendered possible by arresting and releasing the beam, were avoided. It should, however, be noted that the beam was seldom in a state of perfect rest ; generally, the reflected light was moving across the scale to the extent of 1 mm. or 2 mm.

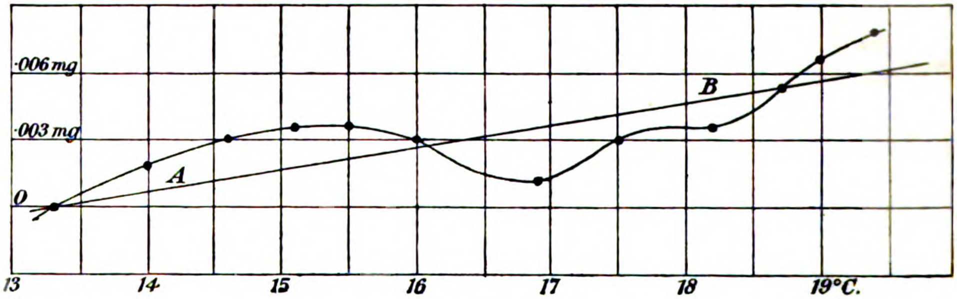


FIG. 2.

On plotting the R.P.'s against correlated temperatures, as in Fig. 2, we obtain a graph representing positive and negative movements about a mean axis *AB*. The experimental results, therefore, support the suggestion already advanced, namely, that with a varying temperature minute but unequal readjustments occur within the attached knife-edge systems. These readjustments appear to be smooth, but they are not uniform. In some cases the L-arm of the balance is lengthened, but in others the R-arm is similarly affected.

From the data given in Table III we find that the balance exhibited for the limits within which it was tested, a mean temperature coefficient *k* equal to +0·008 mg. per 1°C. It must, however, be observed that *k* would almost certainly vary with the load ; and this because some loads assist the relative movements of the knife-edge blocks to a greater extent than do others. It was possible that the changes in the R.P. tabulated above, were in part due to causes which influence the dipping needle. On this point the Astronomer Royal informed me that during April 24 (when the experiments were made), there were " small movements " of the dipping needle at 9 p.m. and again at 11 p.m. Apart from those the needle was undisturbed. The experiments under consideration were all made between the hours of 10 a.m. and 7.35 p.m. ; we, therefore, infer that the difference in the R.P.'s as shown in Table III, were not, to any appreciable extent, due to magnetic disturbances ; hence, in the absence of other evidence, the variations in the R.P. are to be regarded as temperature effects only.

δ. The Influence Exerted by a Magnetic Pole.—The effects produced by varying the magnetic field were investigated as follows :—

Two 10 grm. weights, the one gilded and the other platinized, were chosen, and the value of the former measured in terms of the latter. Using the method of Gauss, a first standardisation was carried out under normal conditions ; this was followed by three others, during each of which a weak and thin magnet 1 m. long, was given a fixed and vertical position. The additional standardisations were effected with the magnet immediately above (1) the L-pan, (2) the centre of the beam, and (3) the R-pan. In each case the lowest pole was distant from the axis of the beam by 14 cm., and its proximity markedly affected the R.P. *Variations* in the new R.P.'s were not, however, greater than those usually observed. The several values found for the standardised weight were as follows :—

TABLE IV.

		Magnet over				
Conditions ...	Normal.	L-pan.	Centre of Beam.	R-pan.	Mean.	Difference between Mean and Normal Values.
Weight ...	$9{\cdot}9988_9$	$9{\cdot}9988_8$	$9{\cdot}9988_4$	$9{\cdot}9988_7$	$9{\cdot}9988_6$	$-0{\cdot}00003 = 1$ in 333000

Considering the exceptional character of the tests, the mean of the three standardisations conducted in the presence of the magnet, is in remarkably good agreement with the value obtained under normal conditions. It, therefore, appears that provided the method of Gauss be used and the two weighings effected within the brief period required, the results obtained with an invar steel beam are but rarely influenced by changes in the earth's magnetism, and even then to a small extent only. Attention may now be directed to the diurnal changes observable in the R.P. of the beam.

ε. Variations Due to Changes in the Earth's Magnetism.—During the experimental work of the preceding sections, there occurred on most days, very distinct changes in the R.P. Occasionally such changes were exceedingly well marked even when the beam had been fully fatigued and left unarrested and the temperature maintained nearly constant ; they were particularly noticeable on April 13, 14, and 15. Replying to my inquiries, the Astronomer Royal stated that on April 14, at 14 h., G.M.T., a " large " magnetic disturbance began, and lasted for approximately 21 hours. In that period the magnetic inclination varied at least 15′ of arc, this variation being five or six times greater than the normal diurnal range.

By calculation I find that during that same period, the maximum variation in the angular displacement of the balance beam was 38′; this is 2·5 times greater than the disturbance recorded at Greenwich. Allowance must, however, be made for the fact that the plane of the balance beam intersected that of the magnetic meridian at an angle of about 45°.

The results tabulated below appear to be of interest in that they illustrate still further the effects producible by magnetic disturbances.

TABLE V.

Date.	Max. Variation in R.P.	Equivalent Angular Variation.	Equivalent Variation in Weight.
April 13, 1926	47	27′	0·155 mg.
April 14, 1926	67	38′	0·220 ,,
April 15, 1926	38	22′	0·125 ,,
April 16, 1926	32	18′	0·105 ,,
April 24, 1926	14	8′	0·046 ,,

It now appeared desirable to obtain some direct information from an inclination needle mounted upon the balance bench. Accordingly, the balance was removed, and a needle 6·5 in. long set up in the plane formerly occupied by the beam. The needle rested upon knife edges, and possessed a high sensitivity; its axis carried a small concave mirror so that deflections could be measured optically. The reflected light was caught upon a millimetre scale placed at a distance of about 2·3 ms.; this, under the circumstances, was the greatest obtainable. In the case of the balance, the distance was 3 ms. Hence, if we multiply the deflections of the needle by the ratio 3/2·3, we at once obtain values directly comparable with the similarly produced deflections of the balance beam. The S-seeking pole was loaded, so that the needle when at rest was horizontal. Errors resulting from draughts were excluded by housing the magnetic system within a glass dome. Thus the conditions under which the needle was placed were as nearly as possible identical with those which had obtained for the balance. The preparations having been completed, frequent observations of the needle were made daily from April 27 to May 8, inclusive. The maximum variations noted for each day during this period are, together with certain equivalent values, set forth in the following table :—

TABLE VI.

Date. 1926.	Greatest Variation.	Variations × 3/2·3.	Variations in Angular Measure.	Variations Expressed as Weight Equivalents.
April 27	6 mm.	7·8 mm.	4·4′	0·026 mg.
28	42 ,,	54·3 ,,	31·0′	0·179 ,,
29	2 ,,	2·6 ,,	1·5′	0·009 ,,
30	6 ,,	7·8 ,,	4·4′	0·026 ,,
May 1	3 ,,	3·9 ,,	2·2′	0·013 ,,
3	27 ,,	34·9 ,,	27·0′	0·115 ,,
4	1 ,,	1·3 ,,	0·8′	0·004 ,,
5	3 ,,	3·9 ,,	2·2′	0·013 ,,
6	3 ,,	3·9 ,,	2·2′	0·013 ,,
7	3 ,,	3·9 ,,	2·2′	0·013 ,,
8	2 ,,	2·6 ,,	1·5′	0·009 ,,

It may be noted that during the period of observation the maxima varied within the limits 31′ and 1·5′ of arc, the mean daily variation being 7·2′. Equivalent variations in the R.P. of the balance, correspond to the respective weights of 0·179, 0·009 and 0·038 mg. These are, therefore, the several apparent variations that a mass of 200 grms. or less might have shown had it been frequently weighed in one pan only. This, of course, is an extreme view. Actually, as for example, in the case of a chemical analysis, weights are determined by a method of difference and within a time that is short: and so in the absence of a "great" and rapidly fluctuating magnetic storm, no appreciable error would be introduced. If, however, circumstances as such that two or more required weighings are in point of time, widely separated, the weight sought can still be accurately determined by having recourse to the method of Gauss; and this holds true notwithstanding marked changes in the magnetic field. We may now conclude with a few remarks having a general rather than a restricted interest.

η. Possible Effects of Convection Currents.—Elsewhere* I have dwelt upon the importance of shielding the pans of high grade precision balances from draughts. The pans of the balance herein considered, were not specially protected: consequently they were liable to be affected whenever the temperature of the room varied. Changes wrought thus are manifested as the following experiments show, by a definite shift in the R.P.

Exp. 1. The room temperature being almost constant, the R.P. was measured and found to be 321.

Exp. 2. When the beam had come to rest, one hand was held against the right-hand glass panel of the balance case. Within a short time the pointer of light travelled to and fro over 15 scale divisions. The new R.P. was 323.

Exp. 3. The preceding Exp. 2 was tried with the left-hand panel of the case. The pointer vibrated to the extent of 9 scale divisions and the R.P. changed to 319.

The maximum difference produced in the R.P. was 4; and this, as the sensitivity of the balance was 304, was equivalent to 0·013 mg.

Convection currents, generated as in Exps. 2 and 3, may be regarded as light and steady winds moving circularly and in a vertical plane. In Exp. 2 the movement is left-handed and in Exp. 3 right-handed. Winds of this kind will in either case tend to steadily depress one pan and at the same time lift the other; hence a left-handed wind will affect the R.P. positively and a right-handed one negatively. All these disturbances are readily and completely excluded by surrounding each pan and its stirrup with a massive brass cylinder.†

The results obtained may be summarized as follows:—

(1) The rigidity of the beam (apart from the knife-edges) is such that fatigue effects are inappreciable.

(2) As a result of high rigidity, the sensitivity of the balance is nearly the same for all loads.

---

* Phil. Trans., A, Vol. 212, p. 237.

† Article "Balance," Thorpe's Dict. of Chem. New Edition.

(3) The beam of invar steel like all others examined by the author possesses a distinct though small temperature coefficient, and this in all probability, varies with the load. The temperature coefficient is almost certainly due to relative movements of the several knife edges and not to differential temperature effects in the beam itself.

(4) The beam tends to behave like a dipping needle and is, therefore, influenced by the earth's and local fields ; but during periods of magnetic constancy, the R.P. of the balance remains unchanged. Hence given a non-varying field, accuracy in weighing is in no way disturbed or minimised.

(5) Errors due to variations in the enveloping magnetic field, may be avoided by weighing according to the method of Gauss.

(6) Provided the precautions indicated are observed, invar steel is, in the author's opinion, an eminently suitable material for the beam of a high-grade precision balance.

I conclude by tendering my best thanks to the Astronomer Royal. Upon two occasions I was supplied with data from the Greenwich Observatory, and in this way very materially assisted.

DISCUSSION.

Prof. D. C. **Miller**, having been called upon by the President, said that as President of the American Physical Society he welcomed this opportunity of conveying to the Physical Society of London the heartiest good wishes of the members of the American society, who follow with the greatest interest the advances made by British physicists.

Dr. E. H. **Rayner** said that he had been reminded by the Paper of an anecdote concerning Mendeleeff, whose influence with the Russian authorities of his day was very great. When the latter wanted scientific information of any kind they applied to Mendeleeff, who sold it at a high price for the benefit of his laboratories. These consequently reached a luxurious level of equipment, and when the Bureau International des Poids et Mesures required a standard metre and kilogramme, the number of significant figures to which the certificate of accuracy was carried did not satisfy Mendeleeff's fastidiousness. Benoît urged, however, that there was in any case no security against some of the microbes on a balance moving along the beam during a measurement, and Mendeleeff was obliged to give way. In the present Paper it would be of advantage if a note on the dimensions of the balance could be added.

Mr. F. A. **Gould** (communicated) : The author's experiments on a balance beam constructed of invar steel are interesting inasmuch as a beam of this material has also been in use at the National Physical Laboratory for over two years. Apart from the three knives, which are of agate, and a rigidly-attached lens-mirror used for reading purposes, the invar beam at the N.P.L. is constructed exclusively of invar steel. It was set up with the object of ascertaining whether it gave an appreciably better performance than a gunmetal beam of similar design and dimensions. In the early stages of construction of this beam its linear coefficient of thermal expansion had been determined at the N.P.L. and found to be 0·0000016 per 1° C. between 0° and 30° C. In view of the occurrence of some cases in which certain alloys purporting to be " invar " have been found at the N.P.L. to have a large coefficient of expansion, it would be useful to know whether the author's beam had been definitely proved, by actual determination of its coefficient of expansion, to be of invar steel.

The tests made at the N.P.L. show that, while good performances have been obtained from the invar beam, experiments on chemical balances of the ordinary designs used by English manufacturers do not give sufficiently conclusive evidence as to whether the properties of invar steel render the use of this alloy desirable in the construction of a knife-edge balance of the utmost precision. In spite of the use of invar, the balance beam of this material at the N.P.L. was found to have a temperature coefficient of the same order of magnitude as those of other balances of ordinary construction. A possible explanation of this is indicated in Mr. Manley's Paper.

Mr. R. S. **Whipple** said that in one of the geodetic surveys a pendulum having rigidly-fixed stellite knife-edges had been employed with success, and in some of the coin-weighing machines used at the Mint the knife-edges actually form part of the beam itself. This feature should be embodied in accurate balances of the future. Possibly a Helmholtz coil would have given a better initation of the earth's field than the means employed by the author.

The author, by way of reply to the discussion, has added at the foot of page 473 some particulars as to the design of the balance.

XLII.—THE SCATTERING POWER OF OXYGEN AND IRON FOR X-RAYS.

By A. A. Claassen, Honorary Research Fellow, University of Manchester.

Received May 26, 1926.

(*Communicated by Prof.* W. L. Bragg.)

Abstract.

The present Paper describes the results of the quantitative measurement of the intensity of X-ray reflexion from different planes of Fe_3O_4. The side of the unit cell $= 8{\cdot}400$ Å. The parameter, fixing the position of the oxygen atoms, has been determined as $x = 0{\cdot}379 \pm 0{\cdot}001$. F-curves, representing the dependance of the scattering power of oxygen- and iron-ions on the glancing angle, have been obtained. These F-curves (uncorrected for heat-motion) decline much more strongly than the calculated curves for Stoner's distribution of electrons amongst atomic levels.

§ 1.

THE dependance of the scattering power on the glancing angle has first been pointed out by Darwin* and Compton† in theoretical Papers on the intensity of reflexion of X-rays. The first detailed examination of the scattering power of atoms has been made by W. L. Bragg, James and Bosanquet‡ in the case of NaCl. They showed that the scattering power F is not a constant, but dies away rapidly with increasing glancing-angle.

Most of the crystal structures determined up till now have been deduced, assuming the scattering power to be constant and equal to the number of electrons in the atom (or ion). For crystal structures involving many parameters however, allowance for the decline with increasing glancing-angle has to be made.

Some information as to the probable amount of this decline can be gathered from the scattering curves calculated by Hartree.§ As appears from the case of NaCl, the experimental decline is stronger than the calculated one, and it will therefore be necessary to determine the experimental decline for as many atoms as possible.

§ 2.

Fe_3O_4 is a member of the spinel-group of crystals. Its structure has been established by W. H. Bragg‖ and S. Nishikawa.¶ The structure is cubic holohedral (space group O_h^7). The elementary cube, containing eight molecules, is built up of face-centred lattices originating in the following points:—

$$
\begin{array}{ll}
8\,Fe^{++} & 0\,0\,0;\ \frac{1}{4}\frac{1}{4}\frac{1}{4} \\[2ex]
16\,Fe^{+++} & \frac{1}{8}\frac{1}{8}\frac{5}{8};\ \frac{3}{8}\frac{3}{8}\frac{3}{5};\ \frac{3}{8}\frac{1}{8}\frac{7}{8};\ \frac{1}{8}\frac{3}{8}\frac{7}{8} \\[2ex]
32\,O^{--} & x\,x\,x;\ x\,\bar{x}\,\bar{x};\ \bar{x}\,x\,\bar{x};\ \bar{x}\,\bar{x}\,x;
\end{array}
$$

$$
\frac{1}{4}-x,\ \frac{1}{4}-x,\ \frac{1}{4}-x;\ \frac{1}{4}-x,\ x+\frac{1}{4},\ x+\frac{1}{4};\ x+\frac{1}{4},\ \frac{1}{4}-x,\ x+\frac{1}{4};\ x+\frac{1}{4},\ x+\frac{1}{4},\ \frac{1}{4}-x.
$$

---

* C. G. Darwin, Phil. Mag., 27, 315 (1914).

† A. H. Compton, Phys. Rev., 9, 29 (1917); 10, 95 (1917).

‡ W. L. Bragg, James and Bosanquet, Phil. Mag., 44, 433 (1922).

§ D. R. Hartree, Phil. Mag., 50, 289 (1925).

‖ W. H. Bragg, Phil. Mag., 30, 305 (1915).

¶ S. Nishikawa, Proc. Tokyo Math. Phys. Soc., 8, 199 (1915).

The side of the unit cell is given by W. H. Bragg as 8·30 Å. A careful determination of the crystal settings for different orders of one plane gave the value 8·400 Å. The value of x has been estimated at about $\frac{3}{8}$, but no accurate determination has been made.

§ 3.

Absolute intensity measurements have been made from (100), (110), (111) and (311) faces. The integrated reflexion was measured in the manner first devised by W. H. Bragg* and described by W. L. Bragg, James and Bosanquet.† In this method the crystal is rotated with uniform velocity through the reflecting angle and the total amount of radiation entering the ionization chamber is measured, allowance being made for general radiation. Each measurement was made in terms of the (400) reflexion of NaCl, for which the absolute intensity was taken as $0{\cdot}94\ 10^{-4}$.‡ The Kα radiation of molybdenum ($\lambda=0{\cdot}7095$ Å) was employed.

TABLE I.

Plane.	Sin θ	$\frac{\varepsilon\omega}{I}10^6$	Structure-amplitude.	S observed.	S calculated.
111	0, 073	8, 1	$8\,\mathrm{Fe}^{+++}-5,66\,\mathrm{Fe}^{++}-5,66\,\mathrm{O}\{\cos(45+3\Delta)-\sin(45+3\Delta)-3\cos(45-\Delta)+3\sin(45-\Delta)\}$	64	59
220	0, 120	27, 4	$8\,\mathrm{Fe}^{++}+16\,\mathrm{O}\{1-\cos 4\Delta\}$	152	153
311	0, 140	52, 5	$8\,\mathrm{Fe}^{+++}+5,66\,\mathrm{Fe}^{++}+5,66\,\mathrm{O}\{\cos(45-5\Delta)+2\cos(45+3\Delta)-\cos(45-\Delta)-\sin(45-5\Delta)-2\sin(45+3\Delta)+\sin(45+\Delta)\}$	230	230
222	0, 146	13, 8	$16\,\mathrm{Fe}^{+++}-8\,\mathrm{O}\{\cos 6\Delta+3\cos 2\Delta\}$	120	118
400	0, 169	56, 0	$16\,\mathrm{Fe}^{+++}-8\,\mathrm{Fe}^{++}+32\,\mathrm{O}\cos 4\Delta$	258	254
333	0, 219	20, 0	$8\,\mathrm{Fe}^{+++}+5,66\,\mathrm{Fe}^{++}+5,66\,\mathrm{O}\{\sin(45-9\Delta)-\cos(45-9\Delta)+3\cos(45+3\Delta)-3\sin(45+3\Delta)\}$	181	178
440	0, 239	85, 5	$16\,\mathrm{Fe}^{+++}+8\,\mathrm{Fe}^{++}+16\,\mathrm{O}\{1+\cos 8\Delta\}$	395	400
622	0, 280	8, 1	$16\,\mathrm{Fe}^{+++}-8\,\mathrm{O}\{\cos 10\Delta+2\cos 6\Delta+\cos 2\Delta\}$	134	130
444	0, 293	11, 0	$16\,\mathrm{Fe}^{+++}-8\,\mathrm{Fe}^{++}+8\,\mathrm{O}\{\cos 12\Delta+3\cos 4\Delta\}$	158	157
800	0, 338	32, 8	$16\,\mathrm{Fe}^{+++}+8\,\mathrm{Fe}^{++}+32\,\mathrm{O}\cos 8\Delta$	301	304
660	0, 359	2, 6	$8\,\mathrm{Fe}^{++}+16\,\mathrm{O}\{1-\cos 12\Delta\}$	87	87
555	0, 366	6, 7	$8\,\mathrm{Fe}^{+++}+5,66\,\mathrm{Fe}^{++}+5,66\,\mathrm{O}\{\sin(45+15\Delta)-\cos(45+15\Delta)-3\sin(45-5\Delta)+3\cos(45-5\Delta)\}$	145	147
666	0, 439	4, 3	$16\,\mathrm{Fe}^{+++}-8\,\mathrm{O}\{\cos 18\Delta+3\cos 6\Delta\}$	132	133
880	0, 478	9, 0	$16\,\mathrm{Fe}^{+++}+8\,\mathrm{Fe}^{++}+16\,\mathrm{O}\{1+\cos 16\Delta\}$	202	204
777	0, 512	—	$8\,\mathrm{Fe}^{+++}-5,66\,\mathrm{Fe}^{++}+5,66\,\mathrm{O}\{\cos(45-21\Delta)-\sin(45-21\Delta)-3\cos(45+7\Delta)+3\sin(45+7\Delta)\}$	—	18
888	0, 585	4, 4	$16\,\mathrm{Fe}^{+++}+8\,\mathrm{Fe}^{++}+8\,\mathrm{O}\{\cos 24\Delta+3\cos 8\Delta\}$	162	162

The two crystals used in this investigation showed (100), (110) and (111) faces. Of these, only the latter face was used directly for the intensity measurements. The other faces, being distorted and striated, had to be ground on with emery. Grinding the natural (111) face had no effect on the observed intensities. In

---

* W. H. Bragg, Phil. Mag., 27, 881 (1914).

† Loc. cit.

‡ From measurements of Wasastjerna.

Table I, column 3, the observed absolute intensities R are given. The accuracy ranges from about 2 per cent. for the stronger reflections to about 5 per cent. for the weakest reflections.

According to Darwin,* the integrated reflection ρ of an ideally imperfect crystal is given by the following expression :—

$$\rho=\frac{\varepsilon\omega}{I}=\frac{4\mu}{N^2\lambda^3}\,\frac{e^4}{m^2c^4}\,\frac{1+\cos^2 2\theta}{\sin 2\theta}S^2e^{-B\sin^2\theta}$$

where N is the number of molecules per c.c. of the crystal, e, m charge and mass of the electron, c the velocity of light, μ the linear absorption coefficient for wavelength λ and including extinction, S the structure-amplitude or number of electrons per molecule efficient in scattering in the direction θ.

The absorption coefficient of Fe_3O_4 has not been determined directly, but can be readily calculated from the values of $\frac{\mu}{S}$ for Fe and O, viz., 36,93 and 1,00 respectively.† From the density of magnetite (5,20) μ is calculated as 141.

Inserting the various numerical values in the above formula, we get :—

$$\rho=\frac{\varepsilon\omega}{I}=1{,}44.\ 10^{-10}\frac{1+\cos^2 2\theta}{\sin 2\theta}S^2$$

in which the heat motion factor is suppressed, so that S really means $Se^{-\frac{B}{2}\sin^2\theta}$ and refers now to eight molecules of Fe_3O_4. From this formula the values of S given in column 5 of Table I are calculated.

In column 4 the structure factors for the different planes are given. As the value of the parameter x differs only slightly from $\frac{3}{8}$, or 135°, this difference $\triangle$ has been used as a new parameter in calculating these structure factors, so that actually $x=135°+\triangle$ when all is expressed in arc measure.

It remains now to determine from these S values, the value of $\triangle$ and the scattering powers of Fe and O.

The iron atoms consist of bivalent and trivalent ones. The nuclear charge for these two kinds of Fe-atoms being the same, the difference in scattering power is only due to a valency electron in the outer layer of the atom. This valency electron, being one of the most loosely bound electrons, will approximately be ineffective as to scattering for larger glancing angles. This fact, that Fe^{++} and Fe^{+++} will be so nearly alike, except for only the very small glancing angles, facilitates the present analysis to a rather large extent.

The value of $\triangle$ being only small, the contribution of oxygen to the structure amplitudes of (220), (311) and (660) may be neglected for a first approximation (*see* Table I). Further, it may be assumed that the scattering power of so light an atom as oxygen has sunk so low for $\sin\theta=0{\cdot}59$ that the (888) reflexion may be regarded as due to iron only. So four points on the Fe-curve have been obtained, by which it is possible to estimate the Fe values for intermediate values of $\sin\theta$. In this way O values can be obtained from the (222), (444), (800) and (666) reflexions, a happy circumstance being the fact that the exact value of $\triangle$ has little or no influence on the magnitude of these structure amplitudes.

---

* C. G. Darwin, Phil. Mag., 43, 800 (1922).

† K. Wingardh, Zeitschr. f. Physik., 8, 363 (1922).

A number of considerations lead to the conclusion that extinction in this particular crystal is very small. It is, of course, most important to determine what part extinction plays in reducing the intensities of the reflexions, because the accuracy of the final results for the scattering powers of oxygen and iron depends on the correct estimation of this factor. If extinction is assumed to be negligible, scattering curves for iron and oxygen can be calculated in the way indicated above, using the reflexions (220), (111) and (666) in the case of iron, and thence deducing the oxygen values from (222), (444), (800) and (666). Now it is found that if these values are used to calculate the intensities for reflexions (400) and (440) the results exactly agree with experiment. These are the two most powerful reflexions given by the crystal, so that if extinction existed it would reduce them much more than any others. The fact that this agreement between calculation and observation exists, indicates that the extinction is, at any rate, small compared with the high absorption coefficient, 141, of the crystal.

This argument may be put in another way. If extinction were appreciable, each S value should be multiplied by $\sqrt{\frac{\mu+\varepsilon}{\mu}}$ in order to get the real value. Here the extinction coefficient ε is equal to $a\rho$, in which a is a constant and ρ the integrated reflexion. This correction has been proved to be valid in the case of NaCl, and Darwin has given theoretical evidence for it. The experimental F curves for iron and oxygen are much lower than those calculated by Hartree. We may seek to explain this by supposing that the strong reflexions are reduced by extinction, and obtain an estimate of the extinction coefficient a by giving it a value which raises the reflexion (440) to that to be expected from Hartree's curves. This involves an increase in the value of F for iron to 17·5 instead of 14. The value of a got in this way is not very large, and the only other S values appreciably increased are those for (311) and (400). The estimated value of the parameter is not altered appreciably. If all the results are interpreted with this estimate of extinction, three points on the curves are raised, whereas the remainder remain where they were. It is obvious from the figure that the F values will now lie on a very irregular curve, so that we are forced to abandon this explanation. We may sum up by saying that everything points to a negligible value of the extinction coefficient.

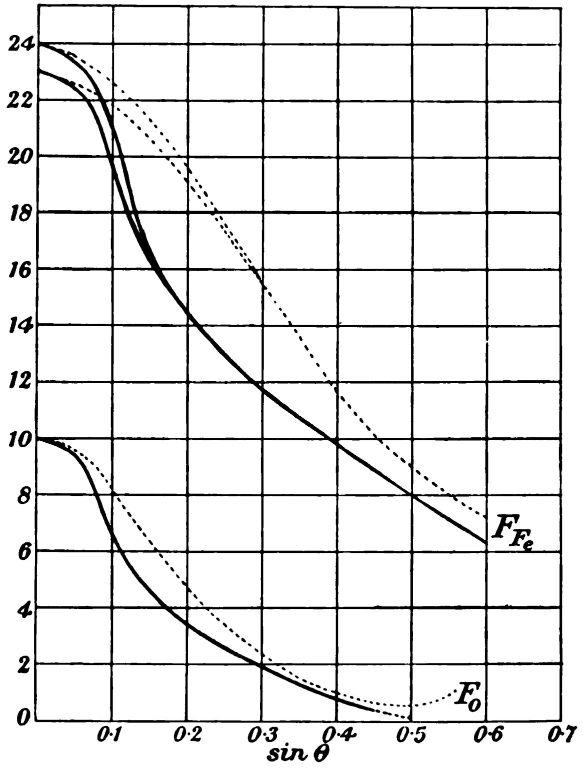
An estimate of $\triangle$ can be made by considering the (111) and (555) reflexions. The structure factor of (555) is very sensitive to small changes in $\triangle$. For $\triangle=0°$ the coefficient in the brackets in Table I is zero; for $\triangle=1°$, 0·7; for $\triangle=1{\cdot}5°$, 1·1; and for $\triangle=2°$, 1·5. Considering the Fe-curve, it follows that S is nearly due to iron only, and that the value of $\triangle$ may not exceed 1·5°. Considering the (333) reflexion, this same limit is found. On the other hand, extrapolating the O- and Fe-curves to $\sin\theta=0$ (ionisation being assumed), it is found that the Fe contribution to (111) amounts to about 50, so that the oxygen contribution is about 14 (which implies that $\triangle$ is positive, as used in the above). Taking the value of $\triangle=1{\cdot}5°$, found above to be the largest one possible, the factor in the brackets becomes 0·25, thus giving a value of about 10 for oxygen. The minimum value of the factor is 0·20. Owing, however, to the exact course of the F-curves for $\sin\theta<0{\cdot}1$ being uncertain, no exacter value for $\triangle$ can be obtained. Thus $\triangle$ is fixed at $136{\cdot}5°\pm0{\cdot}4°$, giving

$x=0{\cdot}379\pm0{\cdot}001$. For $x=0{\cdot}3750$ the oxygen atoms are exactly in cubic close-packing. In column 6 of Table I the calculated values of F from the smoothed F curves are given, using the above value of x. The agreement is very good.

Table II gives the interpolated values of F_0 and F_{Fe} for rational values of sin θ.

TABLE II.

Sin θ	0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60
F	24 23 10	23·3 22·3 9·3	20·9 19·8 6·8	16·5 4·6	14·4 3·4	12·8 2·6	11·7 1·9	10·8 1·3	9·9 0·8	8·9 0·3	8·1 0·15	7·2 ...	6·3 ...



In the figure the dotted lines represent the calculated F curves. The curve for oxygen was calculated by Hartree. The curve for iron was calculated from Hartree's tables. Both curves are based on Stoner's distribution of electrons amongst atomic levels.

It is seen that in both cases the decline is much stronger than the calculated one. For oxygen this has already been made probable by the work of Bradley* and James and Wood.† As in the case of NaCl, probably only part of this can be ascribed to the heat-motion-factor (the curves being really $Fe^{-\frac{B}{2}\sin^2\theta}$ curves). For large glancing angles the difference becomes much smaller. The rising up again of the oxygen curve for sin $\theta > 0{\cdot}45$, as Hartree's calculated curve does, does not seem to take place; otherwise the (888) reflexions would have been observed much stronger. It will be very interesting to see in how far this oxygen curve agrees with the oxygen curve determined from other crystals.

---

* A. J. Bradley, Phil. Mag., 49, 1225 (1925).

† R. W. James and W. A. Wood, Proc. Roy. Soc., 109, 598 (1925).

I am indebted very much to Professor W. L. Bragg, F.R.S., for his kind help and advice and for suggesting this investigation to me.

INDEX.

A

PAGE

Absorption Coefficient for Slow Electrons in Mercury Vapour, The 77
Acoustical Wave Phenomena, The Analogy between Ripples and 234
Ammonia Gas, On the Viscosity of 16
Archer, R. M., *on* Evaporative Losses of Vacuum-Jacketed Vessels of the Dewar Type 247
Atmosphere, Measurement of Ozone in the Earth's 74
Atomic Dimensions 93
Awbery, J. H. (*with* Griffiths, Dr. E.), *on* The Latent Heat of Fusion of some Metals 378

B

Backhurst, Ivor, *on* Obliquity Corrections in Radium Estimation 277
Balances, On the Use of Invar Steel for Precision 473
Benton, W. E., *on* Edge-Tones 109
Bismuth and the Nature of "Raies Ultimes," A Note on λ4722 of 321
Bosanquet, C. E., *on* The Bending of Crystals 88
Brode, Dr. Robert B., *on* The Absorption Coefficient for Slow Electrons in Mercury Vapour 77
Burdon, R. S., *on* The Spreading of One Liquid on the Surface of Another 148

C

Calthrop, J. E., *on* The Effects of Torsion upon the Thermal and Electrical Conductivities of Aluminium, with Special Reference to Single Crystals 207
Capillarity, The Application of Radiography to the Study of 204
Carbon Disulphide, The Refraction and Dispersion of Gaseous 470
Chemical Constant, The Present Status of Theory and Experiment Relating to Specific Heats and the 176
Chree, C., *on* The Times of "Sudden Commencements" of Magnetic Storms: Observation and Theory 35
Claassen, A. A., *on* The Scattering Power of Oxygen and Iron for X-Rays 482
Clarkson, William, *on* The Flashing of Certain Types of Argon-Nitrogen Discharge Tubes 10
Combridge, J. T., *on* The Advance of Perihelion of Mercury 161
Conductivities of Aluminium, with Special Reference to Single Crystals, The Effects of Torsion upon the Thermal and Electrical 207
Crystal Structure of Aluminium, The Effect of Rolling on the 132
Crystals, On the Bending of 88

D

PAGE

Darling, Prof. C. R., Demonstration of Surface Tension Phenomena 275
Davis, Dr. A. H.: The Analogy between Ripples and Acoustical Wave Phenomena 234
Demonstrations:—
- Eastward Deviation of Falling Bodies An Instrument for Imitating the 168
- Kinetic Properties of a Gas Jet 92
- Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material, Application of the 273
- Surface Tension Phenomena 274, 275
- Thermionic Valves, Some Simple Experiments with 335

Dewar Type, Evaporative Losses from Vacuum-Jacketed Vessels of the 247
Diffraction of Light by Spherical Obstacles, **on** The 350
Dimensions, Atomic 93
Discharge Tubes, **on** The Flashing of Certain Types of Argon-Nitrogen 10
Dispersion of Gaseous Carbon Disulphide, The Refraction and 470
Dobson, Dr. G. M. B. (*with* Harrison, D. N.), **on** The Measurement of Ozone in the Earth's Atmosphere 74
Dufton, A. F. (*with* Owen, Dr. E. A.), **on** The Application of Radiography to the Study of Capillarity 204
Dye, D. W., **on** The Piezo-Electric Quartz Resonator and Its Equivalent Electric Circuit 399

E

Eastward Deviation of Bodies Falling from a Great Height, *Demonstration of* An Instrument for Imitating 168
Edge-Tones, On 109
Edser, Edwin, *Demonstration of* Surface Tension Phenomena 274
Edwards, S. G., A.R.C.S. (*with* Worswick, B.), **on** The Viscosity of Ammonia Gas... 16
Electrons in Mercury Vapour, The Absorption Coefficient for Slow 77
Electro-Endosmosis, The Influence of Electrolytes in 363
Electrostatic Machines, The Characteristics of 459
Evans, E. J., **on** The Characteristics of Electrostatic Machines 459

F

Ferguson, Dr. A. (*with* Vogel, I.), **on** The "Hyperbola" Method for the Measurement of Surface Tension 193
Flashing of Certain Types of Argon-Nitrogen Discharge Tubes 10

G

Gas Jet, *Demonstration of* The Kinetic Properties of a 92
Gas at Low Pressures, The Storage of Small Quantities of 129
Gauge, Two New Types of High Vacuum 80
Gravitational Fields, Static and Isotropic 337

PAGE

Griffith, I. O., *on* An Application of Spectro-Photography to the Measurement of High Temperatures 85
Griffiths, A. (*with* Vincent, P. C.), *on* The Viscosity of Water at Low Rates of Flow Determined by a Method of Thermal Convection 291
Griffiths, Dr. E. (*see* Awbery, J. H.)

H

Harrison, D. N. (*see* Dobson, G. M. B.)
Harrison, T. H., *on* Variations in the Thermionic and Photo-Electric Emission from Platinum and Tungsten 214
Hartley, J. J. (*with* Rinaldi, R. H.), *Demonstration of* The Application of the Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material 273
Hartshorn, L., *on* The Properties of Mutual Inductance Standards at Telephonic Frequencies 302
Heat, Critical Discussion of the Determinations of the Mechanical Equivalent of... 169
Hepburn, H. C., *on* The Influence of Electrolytes in Electro-Endosmosis 363
Hodgkinson, T. G., *on* Valve Maintained Tuning Forks 24

I

Inductance Standards at Telephonic Frequencies, The Properties of Mutual 302
Invar Steel for Precision Balances, On the Use of 473

J

Johnson, M. C., *on* The Distribution of Intensity in a Positive Ray Spectral Line... 324

K

King, E. Bolton, *on* Two New Types of High Vacuum Gauge 80
Krishnan, K. S. (*with* Raman, Prof. C. V.), *on* The Diffraction of Light by Spherical Obstacles 350

L

Laby, Prof. T. H.: Critical Discussion of the Determinations of the Mechanical Equivalent of Heat 169
Latent Heat of Fusion of Some Metals, The 378
Liquid on the Surface of Another, The Spreading of one 148
Lowery, H., *on* The Refraction and Dispersion of Gaseous Carbon Disulphide 470
Lunnon, R. G., *on* Atomic Dimensions 93

M

PAGE

Mandell, W., *on* The Measurement of Temperature by Thermocouples in Unequally Heated Enclosures 47
Manley, J. J., *on* The Spectroscopic Detection of Minute Quantities of Mercury...... 127
Manley, J. J., *on* The Storage of Small Quantities of Gas at Low Pressures............ 129
Manley, J. J., *on* The Use of Invar Steel for Precision Balances........ 473
Mather, G. R., *Demonstration of* An Instrument for Imitating the Eastward Deviation of Bodies Falling from a Great Height........ 168
Mechanical Equivalent of Heat, Critical Discussion of the Determinations of...... 169
Mercury, The Advance of the Perihelion of........ 161
Mercury, The Spectroscopic Detection of Minute Quantities of........ 127
Mercury Vapour, The Absorption Coefficient for Slow Electrons in........ 77
Metals, The Latent Heat of Fusion of Some 378
Mutual Inductance Standards at Telephonic Frequencies, The Properties of......... 302

N

Narayan, A. L. (*with* Rao, K. R.), A Note on λ4722 of Bismuth and the Nature of "Raies Ultimes" 321
Narayan, A. L. (*with* Rao, K. R.), *on* The Absorption and Series Spectra of Nickel... 354

O

Obliquity Corrections in Radium Estimation........ 277
Owen, E. A. (*see* Dufton, A. F.)
Owen, E. A. (*with* Preston, G. D.), *on* The Effect of Rolling on the Crystal Structure of Aluminium 132
Ozone in the Earth's Atmosphere, The Measurement of........ 74

P

Perihelion of Mercury, The Advance of the........ 161
Photo-Electric Emission from Platinum and Tungsten, Variations in the Thermionic and 214
Photo-Electric Radiation Pyrometer 69
Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material, *Demonstration of* The Application of the........ 273
Piezo-Electric Quartz Resonator and its Equivalent Electric Circuit, The........... 399
Positive Ray Spectral Line, The Distribution of Intensity in a........ 324
Preston, G. D. (*see* Owen, E. A.)
Pyrometer, A Photo-Electric Radiation........ 69

Q

Quartz Resonator and its Equivalent Electric Circuit, The Piezo-Electric 399

R

PAGE

Radiography to the Study of Capillarity, The Application of 204
Radium Estimation, Obliquity Corrections in 277
" Raies Ultimes," A Note on λ4722 of Bismuth and the Nature of 321
Raman, Prof. C. V., *on* The Diffraction and Series Spectra of Nickel 350
Rao, K. R. (*see* Narayan, A. L.)
Rawlins, F. Ian G., *on* The Present Status of Theory and Experiment Relating to Specific Heats and the Chemical Constant 176
Rayner, E. H., *Demonstration of* Some Simple Experiments with Thermionic Valves 335
Refraction and Dispersion of Gaseous Carbon Disulphide, The 470
Resonator and its Equivalent Electric Circuit, The Piezo-Electric Quartz 399
Rinaldi, R. H. (*see* Hartley, J. J.)
Ripples and Acoustical Wave Phenomena, The Analogy between 234
Rolling on the Crystal Structure of Aluminium, The Effect of 132

S

Scattering Power of Oxygen and Iron for X-Rays, On the 482
Smith, Hugh E., *on* The Influence of Strain on the Thomson Effect 1
Specific Heats and the Chemical Constant, The Present Status of Theory and Experiment Relating to 176
Spectra of Nickel, On the Absorption and Series 354
Spectral Line, The Distribution of Intensity in a Positive Ray 324
Spectro-Photography to the Measurement of High Temperatures, An Application of 85
Spectroscopic Detection of Minute Quantities of Mercury, The 127
Spherical Obstacles, On the Diffraction of Light by 350
Spreading of One Liquid on the Surface of Another, The 148
Storage of Small Quantities of Gas at Low Pressures, On the 129
Strain on the Thomson Effect, The Influence of 1
" Sudden Commencements " (S.C.s) of Magnetic Storms, The Times of 35
Surface Tension Phenomena (*Demonstrations*) 274, 275
Surface Tensions, On the " Hyperbola " Method for the Measurement of 193

T

Temperature by Thermocouples in Unequally Heated Enclosures, The Measurement of 47
Temperatures, An Application of Spectro-Photography to the Measurement of High 85
Temple, Dr. G., *on* Static and Isotropic Gravitational Fields 337
Thermal Convection, Viscosity of Water at Low Rates of Flow Determined by a Method of 291
Thermionic and Photo-Electric Emission from Platinum and Tungsten, Variations in the 214
Thermionic Valves, Some Simple Experiments with (*Demonstration*) 335
Thermocouples in Unequally Heated Enclosures, The Measurement of Temperature by 47
Thomas, Dr. J. S., *Demonstration of* The Kinetic Properties of a Gas Jet 92

PAGE
Thomson Effect, The Influence of Strain on the ... 1
Torsion upon the Thermal and Electrical Conductivities of Aluminium with Special Reference to Single Crystals, The Effects of ... 207
Tuning Forks, Valve Maintained ... 24

V

Vacuum Gauge, Two New Types of ... 80
Vacuum-Jacketed Vessels of the Dewar Type, On the Evaporative Losses from ... 247
Valve Maintained Tuning Forks ... 24
Vincent, P. C. (*see* Griffiths, Dr. A.)
Viscosity of Ammonia Gas, On the ... 16
Viscosity of Water at Low Rates of Flow Determined by a Method of Thermal Convection ... 291
Vogel, I. (*see* Ferguson, Dr. A.)

W

Worswick, B. (*see* Edwards, S. G.)

X

X-Rays, On the Scattering Power of Oxygen and Iron for ... 48

PUBLICATIONS OF THE PHYSICAL SOCIETY.

THE SCIENTIFIC PAPERS

OF THE LATE

SIR CHARLES WHEATSTONE, F.R.S.

Demy 8vo, cloth. Price 12s.; to Fellows, 6s.

Uniform with the above.

THE SCIENTIFIC PAPERS OF

JAMES PRESCOTT JOULE, D.C.L., F.R.S.

Vol. I. 4 Plates and Portrait, price 18*s.*; to Fellows, 9*s.*

Vol. II. 3 Plates, price 12*s.*; to Fellows, 6*s.*

PHYSICAL MEMOIRS.

Part I.—Von Helmholtz, On the Chemical Relations of Electrical Currents. Pp. 110. *Price 6s.; to Fellows, 3s.*

Part II.—Hittorf, On the Conduction of Electricity in Gases; Puluj, Radiant Electrode Matter. Pp. 222. *Price 12s.; Fellows, 6s.*

Part III.—Van der Waals, On the Continuity of the Liquid and Gaseous States of Matter Pp. 164. *Price 12s.; to Fellows, 6s.*

REPORT ON RADIATION AND THE QUANTUM THEORY.

By J. H. JEANS, D.Sc., LL.D., F.R.S.

Second Edition.—*Price 7s. 6d.; to Fellows, 3s. 9d. Bound in Cloth, 10s. 6d.*

REPORT ON THE RELATIVITY THEORY OF GRAVITATION.

By A. S. EDDINGTON, M.A., M.Sc., F.R.S.

Plumian Professor of Astronomy and Experimental Philosophy, Cambridge.

Third Edition.—*Price 6s.; to Fellows, 3s. Bound in cloth, 8s. 6d.; to Fellows, 6s.*

REPORT ON SERIES IN LINE SPECTRA.

By A. FOWLER, F.R.S.,

Professor of Astrophysics, Imperial College of Science, South Kensington, London:

Price to Non-Fellows, 12s. 6d.; to Fellows, 6s. 3d. Bound in Cloth, 15s., to Fellows, 9s.

THE TEACHING OF PHYSICS IN SCHOOLS.

Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

METROLOGY IN THE INDUSTRIES.

Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d

DISCUSSION ON LUBRICATION.

Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

DISCUSSION ON ELECTRIC RESISTANCE. *Price 2s. 6d. net.*

DISCUSSION ON HYGROMETRY. *Price 5s. net.*

DISCUSSION ON IONISATION IN THE ATMOSPHERE. *Price to Non-Fellows, 3s.*

PROCEEDINGS.

The "Proceedings" of the Physical Society can be obtained at the following prices:

Vol. I. (3 parts) bound cloth, 22*s.* 6*d.*

Vols. II., IV., V., XXIII., XXV., XXVI., XXVII., XXVIII., XXIX., XXX. & XXXI. (5 parts each), cloth, 34*s.* 6*d.*

Vols. III., VI. to XII. & XXII. (4 parts each), bound cloth, 28*s.* 6*d.*

Vol. XIII. (13 parts, each containing Abstracts), bound cloth (without Abstracts), 70*s.* 6*d.*

Vols. XIV. & XV. (12 parts, each containing Abstracts), bound cloth (without abstracts), 34*s.* 6*d.*

Vols. XVI. & XIX. (8 parts each), bound cloth, 52*s.* 6*d.*

Vols. XVII., XVIII. & XXI. (7 parts each), bound cloth, 46*s.* 6*d.*

Vols. XX. & XXIV. (6 parts), bound cloth, 40*s.* 6*d.*

Most of the parts can be purchased separately, price 6*s.*, by post 6*s.* 3*d.* Fellows can obtain the *Proceedings* (in parts) for their personal use at half the above prices.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES.

Vols. I. (1895), II. (1896), III. (1897), 22*s.* 6*d.* each; Fellows, 11*s.* 3*d.*

Strong cloth cases for binding the "Proceedings," price 3s. 6d each, post free.

BLAKESLEY, T. H. A Table of Hyperbolic Sines and Cosines. *Price 2s. 3d.; to Fellows, 1s. 2d.*

LEHFELDT, R. A. A List of Chief Memoirs on the Physics of Matter. *Price 3s.; to Fellows, 1s. 6d.*

Applications for the above Publications should be sent direct to

FLEETWAY PRESS, LTD.,

CONTENTS.

PAGE

Title, Contents, Proceedings at Meetings .... i-xix

XXXIII. Static and Isotropic Gravitational Fields. By G. TEMPLE, Ph.D. 337

XXXIV. On the Diffraction of Light by Spherical Obstacles. By Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN 350

XXXV. On the Absorption and Series Spectra of Nickel. By Prof. A. L. NARAYAN, D.Sc., F.Inst.P., and K. R. RAO, M.A. 354

XXXVI. The Influence of Electrolytes in Electro-Endosmosis. By H. C. HEPBURN, B.Sc. 363

XXXVII. The Latent Heat of Fusion of Some Metals. By J. H. AWBERY, B.A., B.Sc., and EZER GRIFFITHS, D.Sc. 378

XXXVIII. The Piezo-Electric Quartz Resonator and its Equivalent Electrical Circuit. By D. W. DYE, B.Sc. 399

XXXIX. The Current-Voltage Characteristics of Electrostatic Machines when Supplying Current to Non-Inductive Loads and to a Coolidge X-Ray Tube. By EVAN J. EVANS, M.Sc. (Lond.) 459

XL. The Refraction and Dispersion of Gaseous Carbon Disulphide. By H. LOWERY, M.Sc., A.Inst.P., F.R.A.S. 470

XLI. On the Use of Invar Steel for Precision Balances. By J. J. MANLEY, M.A. 473

XLII. The Scattering Power of Oxygen and Iron for X-Rays. By A. A. CLAASSEN 482

Index 489

BOUND

APR 8 1927

UNIV. OF MICH.
LIBRARY

UNIVERSITY OF MICHIGAN
3 9015 07790 7700